A Study of the Production of Hydrogen by the Decomposition of Formic Acid over Pd-based and Pt-based Catalysts

Thesis Presented for the award of Doctor of Philosophy (Ph.D.)

By

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Declaration

I declare that the work in this thesis has not been submitted for a degree to this or any other university.

Lijun Jia
23/10/2013
Abstract

As one of main products of acid hydrolysis procedure from biomass, formic acid is a promising hydrogen carrier that has recently been earning more and more attention. CO-free hydrogen production and mild reaction conditions have recently been the two main targets in the production of hydrogen by the catalytic decomposition of formic acid. This thesis reports investigations of the catalytic performance of modified Pd-based and Pt-based catalysts for this reaction.

The doping by alkali metal ions of a C-supported Pd catalyst promotes both its activity and hydrogen selectivity, the effect being in the order: K⩾Cs>Na>Li. The reaction rate is increased by 1-2 order of magnitude using the optimum modified catalyst, 10 wt.% K-Pd/C, and the content of CO in the product is limited to 30 ppm. The apparent activation energy for the reaction increases from a value around 60 kJ mol⁻¹ to 100 kJ mol⁻¹ upon K-doping for both the Pd/C catalyst and a Pd powder catalyst, this showing that the reaction mechanism changes on doping. Based on the activity measurements under both steady state and unsteady state conditions as well as on catalyst characterization results (TEM/EDS, STEM/HAADF, XPS, XRD and TOF-SIMS) and DRIFTS measurements, a reaction mechanism is proposed to explain the results with the K-doped Pd/C catalysts.

Pt-based catalysts supported on N-doped carbon nanofibers (CNFs) have also been studied in formic acid decomposition. The use of CNFs as catalyst supports gives the possibility of controlling the structure of the catalysts during preparation. Nitrogen doping of the CNFs changes the electronic properties and gives more structural defects in the CNFs. Sub-nano-sized Pt particles stabilized by the N-doped CNFs supports have been found to have improved activity in formic acid decomposition and to be inactive in ethylene hydrogenation.
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Publications

1. Pt nanoclusters stabilized by N-doped carbon nanofibers for hydrogen production from formic acid
   *Journal of Catalysis 2013*, 307, pp 94-102

2. Improved hydrogen production from formic acid on a Pd/C catalyst doped by potassium
   Dmitri A. Bulushev, Lijun Jia, Sergey Beloshapkin, Julian R. H. Ross,
   *Chemical Communications 2012*, 48, pp 4184-4186

   Yingnan Zhao, Lijun Jia, José A. Medrano, Julian R. H. Ross, and Leon Lefferts
   *ACS Catalysis 2013*, 3, pp 2341–2352

4. High purity hydrogen production from formic acid on Pd catalysts doped with potassium ions
   Lijun Jia, Dmitri A. Bulushev, Sergey Beloshapkin, and Julian R.H. Ross, in preparation

Presentations (presented by Lijun)

1. Pt Fine Clusters Supported on N-doped Carbon Nanofibers as Active Sites for Hydrogen Production from Formic Acid

2. Formic Acid Derived from Biomass for Hydrogen Production and Ethylene Hydrogenation
   Lijun Jia, Dmitri A. Bulushev, and Julian R.H. Ross, in Summer School of Catalysis for Sustainability in Netherlands, 2011

3. Application of Formic Acid as a Hydrogen Source in Catalytic Hydrogenation Reactions
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Chapter 1
Introduction

1 Hydrogen energy

1.1 Global energy system situation

The worldwide demand for energy dramatically increases with constant growth of the earth’s population and the rising standards of living. The three fossil fuels - coal, petroleum and natural gas - are still playing leading roles in the energy structure although all of them are dwindling at alarming rates. On the other hand, CO$_2$ emissions as the main product from fossil fuel consumption leads to the greenhouse effect. Figure 1 shows that the climate changes over the last century or so have matched the trend of the increased CO$_2$ content in the air. Working towards clean and sustainable energy is an essential topic for all researchers. In this situation, it would be difficult to overestimate the importance of hydrogen energy.

![Figure 1: The changes of global mean temperature and carbon dioxide contents in air; reproduced from reference [1]](image-url)
Robert Hefner of the GHK Company has illustrated changes that have occurred in the global energy structure from 1850 to 1997 and has predicted further changes until 2150; see Figure 2.[2] Since the mid nineteenth century, the world energy has been gradually changing from wood and coal to petroleum and oil and then to natural gas and hydrogen. In other word, the source of energy has been shifting from solids to liquids and then to gases. It is found that the H/C ratio of the energy feedstock increases with the development of renewable energy, the use of which avoids the massive emission of CO₂ into the air. As the only one form of energy that does not involve C, hydrogen energy will inevitably become the main worldwide energy vector in the near future. [2, 3] In January 2003, President Bush in the United States emphasized “the hydrogen economy” in his announcement which stimulated the interest of both the technical community and the broader public in the topic.[4] This initiative embraces a complete hydrogen network including hydrogen production, hydrogen storage and hydrogen use.

Figure 2: Global energy systems transition, 1850-2150; reproduced from reference [2]
1.2 Hydrogen production

The main technologies that have used to produce hydrogen up to now have been summarized by U.S. DOE[4] as follows: (i) reforming of natural gas to hydrogen; (ii) the conversion of coal to hydrogen; (iii) the use of nuclear energy to produce hydrogen; (iv) electrolysis; (v) the use of wind energy to produce hydrogen; (vi) the production of hydrogen from biomass; and (vii) the production of hydrogen from solar energy. Although renewable and sustainable techniques have been developed to quite a reasonable extent, at present 96% hydrogen production still relies on direct reactions of fossil fuels[5] related to hydrocarbon reforming reactions. Table 1 shows the main hydrocarbon reforming reactions for hydrogen production.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>CO₂/H₂ in product</th>
<th>H₂ production from H₂O, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Steam reforming reaction</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_mH_n + mH_2O \rightarrow m\text{CO} + (m + \frac{1}{2}n)\text{H}_2 )</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>( \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2 )</td>
<td>0.25</td>
<td>50.0</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6 + 4\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 7\text{H}_2 )</td>
<td>0.29</td>
<td>57.1</td>
</tr>
<tr>
<td>( \text{C}<em>3\text{H}</em>{12} + 10\text{H}_2\text{O} \rightarrow 5\text{CO}_2 + 16\text{H}_2 )</td>
<td>0.31</td>
<td>62.5</td>
</tr>
<tr>
<td>( \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2 )</td>
<td>0.33</td>
<td>66.7</td>
</tr>
<tr>
<td><strong>Partial oxidation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_m\text{H}_n + \frac{1}{2}m\text{O}_2 \rightarrow m\text{CO} + \frac{1}{2}m\text{H}_2 )</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>( \text{CH}_3\text{OH} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2 )</td>
<td>0.5</td>
<td>/</td>
</tr>
<tr>
<td><strong>Autothermal reforming</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_m\text{H}_n + \frac{1}{2}m\text{H}_2\text{O} + \frac{1}{4}m\text{O}_2 \rightarrow m\text{CO} + \left( \frac{1}{2}m + \frac{1}{2}n \right)\text{H}_2 )</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>( 4\text{CH}_3\text{OH} + 3\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 4\text{CO}_2 + 11\text{H}_2 )</td>
<td>0.36</td>
<td>27.3</td>
</tr>
<tr>
<td><strong>Water gas shift</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 )</td>
<td>1</td>
<td>100</td>
</tr>
</tbody>
</table>
1.3 Sustainable hydrogen source - formic acid

The main obstacles to the development of “the hydrogen economy” are the efficient and safe storage of the hydrogen as well as its transport and distribution due to its low critical point and low density. The preferred techniques currently for hydrogen storage are based on tank systems involving either gaseous pressurized hydrogen or liquid hydrogen. However, the problem is that rather a low hydrogen storage density exists; safety issues should also be considered when high pressure apparatus or high energy liquefaction are adopted. Recently, the concept of hydrogen storage under mild conditions has been put forward. For example, materials based on physisorption of hydrogen (carbon nanotubes, ammonia, doped polymers) have been investigated; in parallel, the use of liquid chemicals as hydrogen carriers (borohydrides, hydrazine, formic acid, etc.) have also received a lot of attention.[3, 7] Formic acid is considered to be one of the most promising hydrogen storage materials due to a number of inherent advantages. As the simplest carboxylic acid, the products of its decomposition are simple and easily controlled.

\[ \text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2 \]

Besides, hydrogen production from the decomposition of formic acid can be obtained under mild conditions. Formic acid contains 4.4 wt.% of hydrogen, this corresponding to a high volumetric hydrogen content: 1 litre of liquid formic acid contains 26.5 moles of hydrogen whereas only 9.8 moles gaseous hydrogen can be stored in 1 liter even at a high pressure of 220 bars. Schmidt[3] has reported a promising hydrogen storage technology which consists of a reaction cycle between carbon dioxide, hydrogen and formic acid. Formic acid is synthesized in this cycle by reducing carbon dioxide and this avoids the extra emission of the greenhouse gas, carbon dioxide.
Formic acid is an important commercial chemical; it has been used as tanning agent in chemical synthesis, as a disinfectant in public stations, and in perfume industry as well. Formic acid is miscible with water and most polar organic solvents. In the vapor phase, formic acid consists of hydrogen-bonded dimers rather than individual molecules (Figure 3); as a result, gaseous formic acid does not obey the ideal gas law.

![Cyclic dimer of formic acid; dashed lines represent hydrogen bonds](image)

**Figure 3:** Cyclic dimer of formic acid; dashed lines represent hydrogen bonds

<table>
<thead>
<tr>
<th>Molar mass</th>
<th>Density</th>
<th>Melting point</th>
<th>Boiling point</th>
</tr>
</thead>
<tbody>
<tr>
<td>46.03 g mol⁻¹</td>
<td>1.22 g ml⁻¹</td>
<td>282 K</td>
<td>374 K</td>
</tr>
</tbody>
</table>

### 1.4 Formic acid production

As early as 1671, natural scientists noticed that ants, specifically red ones, produced an acidic vapour and this was separated by English naturalist John Ray before it was given a name. It was then named formic acid, this coming from the Latin word “Formica” meaning “ant”. It is also known as methanoic acid and is classified as a carboxylic acid. The French chemist Joseph Gay-Lussac was the first to synthesize formic acid from hydrocyanic acid. Later, another French chemist, Marcellin Berthelot synthesized formic acid from CO, this being similar to the method used today: CO is reacted with methanol in the presence of a strong base to produce methyl formate and this is
followed by hydrolysis to produce formic acid. The reactions in this procedure are shown below.

$$ \text{CH}_3\text{OH} + \text{CO} \xrightarrow{\text{Base}} \text{HCOOCH}_3 $$

$$ \text{HCOOCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{Hydrolysis}} \text{HCOOH} + \text{CH}_3\text{OH} $$

Recent formic acid production is mainly based on fossil feedstocks. Reutemaan\cite{8} from BASF reported that the traditional installed formic acid processes mainly consist of methyl formate hydrolysis, oxidation of hydrocarbons, hydrolysis of formamide and preparation of free formic acid from formates. In recent years, most efforts have been made to get formic acid from renewable sources, namely from biomass\cite{9} and CO$_2$ hydrogenation \cite{10, 11}. With the blooming development of renewable energy biomass, formic acid produced from hydrolysis process of biomass is regarded as a feasible method. As discussed by Hayes et al \cite{12}, formic acid is produced in high concentration as a by-product in the production of levulinic acid from cellulose. Considerable work has more recently been done on this process \cite{13-16}. The widely accepted reaction mechanism for this procedure is shown in Figure 4. Cellulose is converted through hydrolysis to produce glucose. Glucose is known to yield hydroxymethylfurfural (HMF) by several dehydrations steps through loss of three water molecules; the presence of a Lewis acid facilitates this process. A rehydration step involving the addition of two water molecules is needed to get equimolar levulinic acid and formic acid production.
Figure 4: Reaction steps of levulinic acid and formic acid production from cellulose; reproduced from reference [15]
2 Early investigations of formic acid decomposition

At the beginning of 20th century, instead of being considered as a hydrogen source, formic acid decomposition was one of the most important model reactions for scientists to test different catalysts and understand how these catalysts work. Both metals and oxides were studied in formic acid decomposition [17-35]. The dehydrogenation and dehydration of formic acid are the two directions of formic acid decomposition (see Figure 5). Hydrogen and CO$_2$ are the products in dehydrogenation reaction while water and CO are the products in dehydration reaction. Between the two set of products, water gas shift (WGS) reaction may take place. Table 3 shows the thermodynamic data of the three reactions in both vapour and liquid phases calculated from HSC chemistry software. Considerable earlier work was reported about the factors which can affect the catalytic selectivity over both metals and metal oxides [18, 24]. Based on the two reaction directions, extensive research was also carried out to understand the catalytic reaction mechanism more fully. In this section, investigations of the heterogeneous catalysts for this reaction in earlier work are summarized.

Figure 5: The reactions between catalytic decompositions of HCOOH and water gas shift reaction
Table 3: Standard thermodynamic data of the three reactions related to formic acid decomposition at 298 K

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^\circ$, kJ mol$^{-1}$</th>
<th>$\Delta H^\circ$, kJ mol$^{-1}$</th>
<th>$\Delta S^\circ$, J mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$HCOOH(g) \rightarrow H_2(g) + CO_2(g)$</td>
<td>-43.4</td>
<td>-14.9</td>
<td>95.6</td>
</tr>
<tr>
<td>$HCOOH(g) \rightarrow H_2O(g) + CO(g)$</td>
<td>-14.8</td>
<td>26.2</td>
<td>137.6</td>
</tr>
<tr>
<td>$H_2O(g) + CO(g) \rightarrow H_2(g) + CO_2(g)$</td>
<td>-28.6</td>
<td>-41.1</td>
<td>-42.0</td>
</tr>
<tr>
<td>$HCOOH(l) \rightarrow H_2(g) + CO_2(g)$</td>
<td>-34.9</td>
<td>29.3</td>
<td>215.5</td>
</tr>
<tr>
<td>$HCOOH(l) \rightarrow H_2O(l) + CO(g)$</td>
<td>-14.9</td>
<td>26.4</td>
<td>138.6</td>
</tr>
<tr>
<td>$H_2O(l) + CO(g) \rightarrow H_2(g) + CO_2(g)$</td>
<td>-20.0</td>
<td>2.9</td>
<td>76.9</td>
</tr>
</tbody>
</table>

2.1 Catalytic performance

2.1.1 Formic acid decomposition over Cu and Ni based catalysts

Ying and Madix [36] found that only carbon dioxide and hydrogen were produced from formic acid decomposition on Cu (110) and showed that the rate limiting step is the decomposition of adsorbed formate. Later, Iglesia and Boudart [37-40] reported work on the catalytic decomposition with Cu, Ni and copper-nickel alloys as catalysts. They prepared supported Cu, Ni and Cu-Ni alloy catalysts and found that a formate ion was intermediate in both the dehydrogenation and dehydration reactions, while formic anhydride existed as another intermediate when HCOOH became preadsorbed at low coverage on CuNi single crystals. The existence of these two intermediates was related to the surface structure of catalysts; the formate ions adsorbed on two adjacent Ni atoms while formate anhydride needed four sites. Boudart [40] confirmed that formate intermediates were preferred in the catalytic decomposition of HCOOH on Ni.
Subsequently, Iglesia and Boudart [41] reported that neither formic acid dehydrogenation nor dehydration is a structure sensitive reaction. The rates of the two reactions and the decomposition selectivity are not affected by Ni dispersion or Ni particle size. The decomposition selectivity was only controlled by entropy changes between two reaction paths since the activation energy of these two paths were similar. Ito and Suetaka [42] studied HCOOH decomposition using IR spectroscopy with Ni and Cu surfaces and verified again the existence of formate and formic acid anhydride as intermediates based on the peaks of asymmetric and symmetric OCO stretching bands and COC stretching bands. On the basis of the work mentioned above, Dubois et al [43] further investigated the kinetics of formic acid decomposition on a Cu surface with electron energy loss spectroscopy (EELS). Two different adsorbed states, formate species symmetrically bonded to Cu surface with normal orientation and hydrogen bonded to Cu surface with a tilted orientation that could be a mixed array of formate and formic acid molecules, were confirmed on Cu (100) under UHV conditions. At high surface coverage, the activation energy of formic acid dehydrogenation decreased, this being explained by the appearance of canted, hydrogen-bonded species.

**2.1.2 Formic acid decomposition over Pd and Au based catalysts**

Thermal desorption spectroscopy (TDS) and Fourier transform reflection absorption infrared spectroscopy (FT-RAIRS) were used by Erley [44] to understand the behavior of adsorbed HCOOH on Pd (100). He found that adsorbed formic acid on Pd (100) started to decompose at 170 K and completely converted into adsorbed CO, hydrogen, and oxygen; only small amount of formic acid decomposed into CO$_2$ and H$_2$O. It is interesting that no evidence of intermediates was found during the decomposition.
Almost at the same time, Solymosi [45] studied the adsorption and reaction of HCOOH on both clean and K-promoted Pd (100) surfaces. As in the work done by Erley, Solymosi found that strongly adsorbed HCOOH species were obtained on clean Pd (100) at low exposures; most of the adsorbed HCOOH decomposed into H\textsubscript{2}, CO and small amounts of H\textsubscript{2}O below 200 K; no evidence was found for the formation of formate. In contrast, with potassium-doped surfaces, formate species were detected by ultraviolet photoelectron spectroscopy (UPS) and an explanation that formic acid interacts directly with potassium adatoms to decompose was proposed.

### 2.2 Reaction mechanism of formic acid decomposition

Mars et al [18] reviewed the kinetics and mechanisms of both the catalytic dehydrogenation and dehydration reactions on heterogeneous catalysts in 1963. They showed that both catalytic decomposition directions proceed via an intermediate formate ion. The kinetics of reaction are given by a first-order expression (e.g., on Ag and Au) when step A of Figure 6 is rate determining whereas zero-order kinetics appeared (e.g., on metals such as Pt, Ir, Ru, Pd and oxides) when steps B or C are the limiting ones. The latter situation happens quite often when the stability of chemisorbed formate on the catalyst surface is high. They also found that in the zero-order region, there is close relation between the catalyst activity and the stability of the bulk formates. Similar reaction rates of the order $10^{14}$ molecules cm\textsuperscript{-2} sec\textsuperscript{-1} in formate disassociation were obtained at the temperature just above the decomposition temperature of corresponding bulk formate.
These authors also discussed the different formate adsorption modes, an essential step in understanding the mechanism of the preferred decomposition direction. Figure 7 shows the interconversion between the two different formate states. With the assumption of monomolecular decomposition, the stronger the bond existing between the oxygen and the metal, the greater the probability of dehydration. In contrast, dehydrogenation will be favored when there is an affinity between the metal and hydrogen.

In a paper published prior to that by Mars et al, Fahrenfort, Van Reijen and Sachtler explored 1960[46] the concept of a volcano curve for formic acid decomposition. Based on the concept of the formation of a formate as an intermediate, a curve was plotted to
relate the heat of formation ($\Delta H_f$) of the metal formate salt and the temperature at which the reaction reaches a specific rate. Figure 8 shows that Pt, Ir, Pd and Rh are good catalysts for formic acid decomposition due to the heat of formate formation being neither too high nor too low; in contrast, Au, Ag, Co and Fe are not good catalysts in this reaction as a high activation energy for formate adsorption is needed on Au, Ag while a high desorption energy is needed with Co and Fe. The volcano curve based on formic acid decomposition study was a milestone in catalysis development as it stressed the first time the importance of surface species in determining the rates of catalytic reaction.

![Volcano plot for the decomposition of formic acid on transition metals](image)

**Figure 8:** Volcano plot for the decomposition of formic acid on transition metals; reproduced from reference[47]
3 Recent development on hydrogen production from catalytic decomposition of formic acid over heterogeneous catalysts

Since the application of hydrogen energy began to be considered as a possible issue, most researchers working on the decomposition of formic acid started to focus on CO-free hydrogen production from formic acid under ambient conditions. Unlike the early work in which the reactions were always carried out at temperatures over 373 K, leading to high concentration of CO in product, researchers have recently tried to control reactions at as low a temperature as possible in order to produce more pure hydrogen according to the thermodynamic equilibrium to meet the requirements of fuel cell application. There are many advantages to the use of heterogeneous catalysts: for example, easy separation for recycle use; and suitability for application in fixed bed reactors for continuous processes. Investigations of the decomposition of formic acid over heterogeneous catalysts started in the 1930s; most current work is also based on heterogeneous catalysts.

3.1 Catalytic performance

3.1.1 Formic acid decomposition over Pd-based catalysts

Table 4 summarizes the heterogeneous catalysts that have been studied and the corresponding performances for the decomposition of formic acid. Most noble metals, Pd, Ag, Ir, Pt and Au, have been used as active components of the heterogeneous catalysts for this reaction; contrarily, metal oxides have rarely been used in recent years because they often lead to high CO production. In previous work in our lab, Bulushev [48, 49] reported the performance of Pd/C catalysts for formic acid decomposition in
the vapor phase. A turnover frequency ($TOF = \frac{\text{Molescles formed}}{\text{Metal active site}}$) of 255 h$^{-1}$ with a selectivity of 99 % was obtained at 373 K. The CO concentration in the product obtained in this work was not low enough for direct fuel cell applications. However, Bulushev et al found that both the selectivity and activity of Pd/C catalysts were improved by the introduction of water vapor.

Pd catalysts on various supports have been used in the catalytic decomposition of formic acid [50-54] and it has been found that the supports can significantly affect the catalytic performances. Bowker et al investigated formic acid decomposition over TiO$_2$ and Pd/TiO$_2$ and reported that only the dehydration reaction took place on TiO$_2$, no dehydrogenation reaction occurring without Pd. In addition, they also found that the rate of formic acid decomposition over Pd/TiO$_2$ is slower than over a Pd single crystal.

Wang et al[55] have reported work on formic acid decomposition in the aqueous phase over a Pd/C catalyst. The reaction was carried out at room temperature in the presence of sodium formate in the reaction solution. The advance made in this work is that no CO product was detected in either an MS or GC; this would permit the practical application of the formic acid system in fuel cells. (Any CO formed as a side product would be a poison the catalysts in fuel cells, such as Pd and Pt.) Loges et al[56, 57] and Fellay et al[58] reported 100% hydrogen selectivity in formic acid decomposition in the presence of homogeneous catalysts. On the basis of these investigations, Zhao et al[59] attempted to combine organometallic complexes and heterogeneous catalysts together and to use the composite catalysts in formic acid decomposition in order to avoid CO production. They modified silica supports and obtained functionalized silica following depositing noble metal on it. With an immobilized catalyst, Pd-S-SiO$_2$, a TOF of 719 h$^{-1}$ and $\approx$ 100%
hydrogen selectivity in the decomposition of formic acid in aqueous medium was obtained.
Table 4: Catalytic performance of heterogeneous catalysts in hydrogen generation from formic acid decomposition

<table>
<thead>
<tr>
<th>Catalyst (vapor phase)</th>
<th>TOF, h⁻¹</th>
<th>Selectivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1wt.% Pd/C</td>
<td>255 at 373 K</td>
<td>≈ 99% at 373 K</td>
<td>[48, 49]</td>
</tr>
<tr>
<td>10%K-1%Pd/C*</td>
<td>972 at 343 K</td>
<td>≈ 99.8% at 343 K</td>
<td>[60]</td>
</tr>
<tr>
<td>1 wt.% Au/SiO₂</td>
<td>7024 at 473 K</td>
<td>93.7% at 473 K</td>
<td>[61]</td>
</tr>
<tr>
<td>1 wt.% Au/TiO₂</td>
<td>57.6 at 373 K</td>
<td>&lt; 70% at 373 K</td>
<td>[48]</td>
</tr>
<tr>
<td>0.8 wt.% Au/C</td>
<td>21.6 at 373 K</td>
<td>≈ 90%-95% at 433-623 K</td>
<td>[48]</td>
</tr>
<tr>
<td>0.61 wt.% Au/Al₂O₃</td>
<td>2010 at 353 K</td>
<td>&lt; 10 ppm CO at 353 K</td>
<td>[62]</td>
</tr>
<tr>
<td>0.5 at%, 0.03 at% Au/CeO₂</td>
<td>2268 at 403 K</td>
<td>100% at 353 K</td>
<td>[63]</td>
</tr>
<tr>
<td>2 wt.% Pt/Al₂O₃</td>
<td>306 at 353 K</td>
<td>n/a</td>
<td>[62]</td>
</tr>
<tr>
<td>Mo₂C/C</td>
<td>437 at 423 K</td>
<td>95-98% at 423 K</td>
<td>[64]</td>
</tr>
</tbody>
</table>

* The results produced from this thesis
Table 4: Catalytic performance of heterogeneous catalysts in hydrogen generation from formic acid decomposition (continued)

<table>
<thead>
<tr>
<th>Catalyst (aqueous phase)</th>
<th>TOF, h⁻¹</th>
<th>Selectivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>160 at room temperature</td>
<td>CO-free hydrogen production at room temperature</td>
<td>[55]</td>
</tr>
<tr>
<td>Pd-S-SiO₂ (S: sulphate)</td>
<td>719 at 358 K</td>
<td>no CO detected at 358 K</td>
<td>[59]</td>
</tr>
<tr>
<td>Ir/C</td>
<td>345.6 at 373 K</td>
<td>≈ 99.0% at 423 K</td>
<td>[65]</td>
</tr>
<tr>
<td>Co₀.₃₀Au₀.₃₃Pd₀.₃₅/C</td>
<td>80 at 298 K</td>
<td>100% at 298 K</td>
<td>[66]</td>
</tr>
<tr>
<td>Au/ZrO₂</td>
<td>1590 at 323 K</td>
<td>CO-free hydrogen production at 323 K</td>
<td>[67]</td>
</tr>
<tr>
<td>20 wt% PdAu/C-CeO₂</td>
<td>832 at 375 K</td>
<td>&lt; 140 ppm CO at 375 K</td>
<td>[68]</td>
</tr>
<tr>
<td>PdAu@Au/C core-shell</td>
<td>n/a</td>
<td>30 ppm CO at 356 K</td>
<td>[69]</td>
</tr>
</tbody>
</table>
3.1.2 Formic acid decomposition over Au-based catalysts

According to the early volcano curve theory on catalytic activity of the transition metals in formic acid decomposition, gold would not be a good catalyst for the reaction as the activation energy of formate formation is too high. Bulushev reported that both carbon and TiO$_2$ supported Au catalysts showed very low activity in formic acid decomposition with TOF values of 21.6 h$^{-1}$ and 57.6 h$^{-1}$ at 373 K, respectively, much lower than that over Pd/C catalyst. The hydrogen selectivity over the Au/C sample was lower compared with Pd/C while, with a 1% Au/TiO$_2$ catalyst, the hydrogen selectivity did not exceed 70% over quite a broad temperature range and continued to decrease with an increase in temperature. The low selectivity with Au/TiO$_2$ was explained by the use of the TiO$_2$ support as this oxide gives the dehydration reaction.

In contrast to these results, the catalytic reactivity is better with small Au clusters on oxide supports than that with large Au clusters, this being explained by Ojeda and Iglesia[62] to result from stronger binding between reacted molecules and the unsaturated species of Au metal, anions, or cations. They reported results obtained with a Au/Al$_2$O$_3$ catalyst, this giving outstanding performance with TOF as high as 2010 h$^{-1}$ at 353 K for formic acid decomposition. Figure 10 shows a comparison of results obtained over Al$_2$O$_3$ supported Au and Pt catalysts. The turnover rate on the Au/Al$_2$O$_3$ was much higher than that on the Pt/Al$_2$O$_3$ at 343-383 K and the difference increased with lower reaction temperature. Ojeda and Iglesia attributed the high activity and selectivity to well-dispersed Au species undetectable by TEM. On the base of the results, they proposed two plausible pathways for HCOOH dehydrogenation on well dispersed Au species which also proceed via formate. The products contain less than 10 ppm CO suitable for direct application of fuel cell.
Some very recent work on Au-based catalysts supported on CeO₂ achieved CO-free hydrogen production from the dehydrogenation of formic acid[63]. Flytzani et al have a different explanation to that proposed by Ojeda and Iglesia involving TEM-invisible gold species as active sites for the adsorption of formate species in formic acid decomposition. They proposed instead a reaction pathway involving a methyl formate (HCOOCH₃) species as intermediate as this allowed them to explain the lack of CO production without involving the WGS reaction in the mechanism. They concluded that the high stable activity with a TOF of 2268 h⁻¹ at 403 K obtained with Au/CeO₂ made it a promising catalyst for formic acid dehydrogenation in practical applications.

Solymosi[61] also reported work on Au catalysts used for formic acid decomposition and compared the performance using different supports (see Figure 10). They found that dehydrogenation was predominated on Au catalysts supported on SiO₂, CeO₂ or Norit carbon whereas dehydration was favored on those supported on Al₂O₃, ZSM-5, and TiO₂. All activity experiments of formic acid decomposition in this work were carried
out in quite a high range of temperature and this could have resulted in low hydrogen selectivity. The paper is vague about the hydrogen selectivity over 1% Au/SiO$_2$: based on a calculation with the TOF$_{H_2}$ and TOF$_{HCOOH}$ data reported in the paper, it is 93.7%; however, the abstract of reference 61 says that CO-free hydrogen was obtained on 1% Au/SiO$_2$ at 383-473 K. However, the introduction of water to the formic acid (which was also called “reforming of formic acid” in the paper) enhanced the hydrogen selectivity, particularly at high temperature.

![Figure 10: Temperature dependence of conversion and hydrogen selectivity of formic acid decomposition over supported Au catalysts; reproduced from reference[61]](image)

Au based catalysts have also been examined for liquid phase formic acid decomposition. Bi et al[67] reported work on formic acid decomposition in a FA-amine mixture over an
Au/ZrO$_2$ catalyst. TOF values of 1590 h$^{-1}$ at 323 K and 252 h$^{-1}$ at room temperature were obtained, with CO-free hydrogen production.

### 3.1.3 Formic acid decomposition over multi-metal based catalysts

The addition of a second metal to a catalyst is a common method to alter the electronic properties of the active phase in order to improve its catalytic performance. In the research on formic acid decomposition, work with two metal components has been done by using metal alloys[50, 68] or physical mixtures of metals[45, 51, 60, 70] or even by creating core-shell type metal particles[69, 71, 72]. As an example, Xing[68] and his co-workers synthesized Pd-Au/C and Pd-Ag/C alloy catalysts with particle sizes of 3.5 nm (Pd-Au) and 8 nm (Pd-Ag) for hydrogen production from the decomposition of formic acid. They found that both Au and Ag have a significant effect on the stability of Pd nanoparticles in an aqueous phase. With the introduction of copper group metals, a lower CO concentration (< 80 ppm CO) was observed in the product at 365 K. Furthermore, the catalytic activity was dramatically increased when CeO$_2$ was introduced as a promoter. In the system of Pd-Au/C-CeO$_2$ ($n_{\text{Pd}} : n_{\text{Au}} = 1 : 1$), TOF values of 227 h$^{-1}$ at 365 K and 832 h$^{-1}$ at 375 K were achieved; the TOF 27 h$^{-1}$ in the absence of CeO$_2$ at 365 K. In a subsequent study, these authors introduced a rare earth elements (Dy, Eu and Ho) into the catalytic system described above and obtained further promotion[73]. In contrast to these results, work in our lab on a PdAu/Al$_2$O$_3$ alloy catalysts did not show any improvement in the catalytic decomposition of formic acid when compared with a single metal Pd/Al$_2$O$_3$ catalyst[50]; in this work, relatively large metal particles were present (>10 nm) and a surface alloy of constant composition Pd$_2$Au was formed over a wide range of Au fractions, from 0.33 to 0.87 (see Figure 11).
The TOFs of this alloy based on the Pd surface concentration were 2-3 times lower than that for a Pd/Al₂O₃ catalyst.

Figure 11: The surface and bulk composition of PdAu particles with different content of Au; reproduced from reference[50]

In a similar work by Huang et al[69], a PdAu@Au/C core-shell nanostructure catalyst was synthesized by a simultaneous reduction method without any stabilizer. Around 75% particles were in the size range of 10-20 nm and the average particle size was around 16nm. In contrast to the work of Bulushev et al, it was argued that the Au atoms were dispersed over the surface of all the particles while Pd atoms were only located in the center of the particles; in other words, the surface of bimetallic PdAu@Au/C catalysts was pure Au. Huang et al. indicated that both the activity and stability of the catalyst were improved compared to the monometallic Au/C and Pd/C samples measured under the same conditions (see Figure 12). Unfortunately, no TOF data were reported in their paper.
In order to decrease the consumption of noble metals as catalysts in formic acid decomposition, Jiang and his co-workers prepared a catalyst consisting of a CoAuPd alloy supported on C for hydrogen generation from formic acid. They reported a TOF of 80 h$^{-1}$ with 100% hydrogen selectivity, with excellent stability to formic acid decomposition, at 298 K (room temperature). They claimed that the initial TOF value was the highest value ever reported over a heterogeneous catalyst without any additive at room temperature.

**3.1.4 Formic acid decomposition over non-metal based catalysts**

Until now, the only competitive alternative to noble metal catalysts with a similar activity and hydrogen selectivity is a Mo$_2$C catalyst reported by Solymosi et al.[64]. In
this work, they studied Mo$_2$C supported on carbon nanotubes (CNT) and carbon Norit over a temperature range from 350 to 750 K for both the decomposition and steam reforming of formic acid. The catalyst 1% Mo$_2$C/C achieved complete formic acid conversion at 423 K with a hydrogen selectivity between 95 and 98% and this was considered as the most promising catalyst to replace noble metal ones. As with their Au catalysts[61], the addition of water to the formic acid effectively promoted the hydrogen selectivity, this probably being due to a shift in the WGS equilibrium towards H$_2$/CO$_2$.

### 3.2 Catalytic mechanism of formic acid decomposition

A study of the mechanism of a catalytic reaction helps in the optimization of both catalysts and reaction conditions and this is true also of work on formic acid decomposition. In this section, some acceptable reaction mechanisms on various heterogeneous catalysts are summarized, these being based on the both experimental and theoretical work.

#### 3.2.1 The adsorption states of formate on noble metals

Density functional theory (DFT) is a quantum mechanical modelling method to investigate the electronic structures of many systems, in particular atoms, molecules, and the condensed phases. Quite an amount of calculation work based on DFT has been done to further understand the reaction mechanism by modelling and comparing details of adsorbed reactants, possible reaction intermediates and reaction pathways.

Hu et al[74] investigated HCOOH decomposition mechanisms in both the gaseous and aqueous phases over four common noble metals (Pt, Pd, Rh, and Au) using the DFT calculation method. In this work, they compared for gas phase HCOOH decomposition on the (111) surfaces of these four noble metals three different pathways: (i) the direct
pathway from HCOOH to CO$_2$ or CO; (ii) a pathway in which HCOOH goes first via C-H bond scission to form COOH, this being followed by further O-H bond scission; and (iii) a pathway involving HCOOH dehydrogenation to HCOO followed by C-H bond breaking. The modelling results showed that both the first two reaction pathways are kinetically hindered by high activation barriers. The third pathway is the widely accepted one involving formic acid decomposition via a formate as an intermediate.

An adsorption structural study of formate was done by Outka and his co-workers [75, 76]. They investigated the adsorbed mode of formate on Cu (100) and Cu (110) and reported that an aligned-bridge mode exists on both Cu crystal surfaces. They also proposed another adsorption mode on Cu (100) in which the formate occupies a cross-bridging site with the O-O direction parallel to the surface in such a way that the O-O atoms take up the off-hollow sites on the Cu surface (as shown in Figure 13). This geometry turned out to be incorrect: the O-O atoms should be adsorbed atop on Cu surface atoms[77].

Figure 13: Adsorbed formate species on Cu (110) and Cu (100); reproduced from reference[77]
Four common adsorption modes of formate on noble metals are illustrated in Figure 14. Here, the definitions often used in previous references [74, 78-80] for these four binding modes are summarized. Unidentate is used to describe the adsorption state of formate with one oxygen atom interacting with one metal atom while bidentate stands for the situation in which two oxygen atoms of the formate species interacts with one metal atom. The modes involving both a single oxygen atom and two oxygen atoms adsorbed on two metal atoms are termed bidentate bridging modes.

**Figure 14**: Schematic representation of formate binding modes on noble metals: (a) unidentate, (b) bidentate, (c) bidentate bridging (HCOO*$_{bod}$) and (d) another bidentate bridging (HCOO*$_{boh}$); reproduced from reference[74, 78-80]

Four decades after the volcano-curve approach of Fahrenfort et al, Wachs[81] pointed that the properties of bulk metal formate used as x-axis in volcano curve are not inherently related to the stability of the surface reaction intermediate as no bulk metal formate is formed, rather surface formates; in other words, the properties of the bulk formates cannot be used directly to predict the rate of a catalytic reaction on the corresponding catalyst metal. Barteau et al [82, 83] plotted a Figure showing relationship between the temperature of formate decomposition on metal surfaces and the standard enthalpy of formation for the corresponding metal oxide per mole of metal (see Figure 15). They/he showed that the decomposition temperatures of formate over
metals in both group IB and group VIII follow linear correlations with the heats of formation of the corresponding metal oxides. The intercept of the line representing IB metals is higher, this indicating that these metals are less active for C-H cleavage.

![Figure 15](image-url)

**Figure 15**: Correlation of formate decomposition temperatures on metal surfaces with the corresponding heats of formation of the metal oxides; reproduced from reference [82]

### 3.2.2 Catalytic reaction mechanism of formic acid decomposition over single metal based catalysts

The reaction steps proposed by Hu et al[74] are as follows: gas-phase HCOOH molecules approach and adsorb on the surface as HCOOH*, these preferring to produce H* and bridging HCOO*\(_{\text{boob}}\) intermediates on the four noble metal atoms as in the binding state shown in Figure 14c; the HCOO*\(_{\text{boob}}\) then undergoes a transformation to another type of bidenate bridging HCOO*\(_{\text{boob}}\) mode (Figure 14d) with one oxygen interacting with two metal atoms on the surface; this is then decomposed into CO\(_2\) and
another H* (see Figure 16). The rate controlling step in this mechanism is the transformation of bidentate HCOO*$_{boob}$ to HCOO*$_{bob}$ on Pd, Pt and Rh; on Au, it is the step of dissociation of HCOOH* into HCOO*$_{boob}$ and H*. For an aqueous phase, Hu et al concluded that HCOOH reacts with liquid water to form a solvated proton and aqueous HCOO$. Adsorbed HCOO$_-$ on noble metal surface produces CO$_2$, this existing as carbonic acid before being released by dissociation of the C-H bond. The adsorbed H* diffuses from an fcc site to an atop site via a bridge site to form gas phase H$_2$. The rate limiting step on Pt (111) is the combination of two H* to give gas phase H$_2$ while that on Pd (111) is H* diffusion from a bridge to an atop site.

Figure 16: Scheme of the reaction mechanism for gas-phase formic acid decomposition on (111) surfaces of the noble metals; reproduced from reference[74]
Figure 17: Elementary reaction of preferred pathway for dehydrogenation of formic acid on a Pd (111) surface; reproduced from reference [84]

Zhou et al[84] reported a theoretical study using DFT of the adsorption and dehydrogenation of formic acid on a Pd (111) surface. This work showed two adsorption modes of HCOOH, an “on top” mode and a “bridge” mode. The preferred pathway of dehydrogenation of HCOOH started from the “bridge” mode shown in Figure 17. The whole process is described as follows:

\[
HCOOH \rightarrow HCOO_{bridge} \rightarrow HCOO_{on\ top} + H ,
\]

\[
HCOO_{on\ top} \rightarrow HCOO_{bridge} \rightarrow CO_2 + H .
\]

Luo and his co-workers[85] also published modelling results for formic acid dehydrogenation on Ni (111). They found that formic acid prefers to be adsorbed on the
Ni (111) surface nearly perpendicular with the oxygen atom (O=C) atop and the hydrogen atom (H-O) bridging two neighboured Ni atoms shown in Figure 18, this being similar to the modelling results on Pd (111) of Zhou et al. Formate was considered to be an intermediate and to adsorb in a bidentate bridging structure with its two oxygen atoms (O-C-O) on the Ni atoms. Formate dehydrogenation into carbon dioxide and hydrogen atom was again confirmed as the rate-determining step on the Ni (111) surface. The calculations on Ni (111), Pd (111) and Pt (111) were compared and it was found that all three metal surface show significant similarities in their catalytic properties. In addition, the calculated reaction barrier for formic acid dehydrogenation is the lowest on the Pd surface, followed by Ni and Pt.

![Figure 18](image)

**Figure 18:** Schematic representation of formic acid dehydrogenation on Ni (111); reproduced from reference[85]

### 3.2.3 The effect of water on formic acid decomposition

Savage et al[86] studied the role of water in formic acid decomposition using ab initio quantum chemical calculations and found that water acts as a homogeneous catalyst, decreasing the activation barriers for both dehydration and dehydrogenation. Based on their calculation, they argued that water molecules facilitate the bond breaking and bond
forming to accelerate product formation. This work confirmed the positive effect of water in formic acid decomposition; however, this only simulated reactions involving one and two water molecules, this being quite different from the reactions in real aqueous solutions.

3.2.4 The promotion by the introduction of alkali metals into catalysts

The introduction of a second metal into a catalyst frequently promotes the catalytic performance and attempts have been made to find suitable promoters for formic acid decomposition. Solymosi[45] compared the adsorption and reaction of HCOOH on both pure and K-promoted Pd (100) surfaces and found that formate did not form on clean Pd (100). Two decades ago, Solymosi and Kovacs[87] reported on the adsorption and reaction of formic acid on K-promoted Pd (100) surfaces. At a temperature below 200 K, formic acid adsorbed on a clean Pd (100) and generated CO and H₂; no evidence was found for the formation of formate. However, doped potassium induced the formation of formate species, a stable formate (HCOOK) being produced from the reaction between formic acid and the potassium adatoms. In addition, they found that the surface decomposition pathway and product distribution were changed. CO, CO₂ and H₂ were stabilized as products by the potassium.

Davis and his colleagues [88, 89] reported the catalytic links and similar mechanisms for the formic acid decomposition and WGS reactions over both Pt/ceria and Pt/thoria in the presence of water. Both of these two reactions proceed via formate intermediates. With Pt catalysts supported on these two oxides, the active sites for both WGS and formic acid decomposition are related to partial reduction of the oxides surface at positions where bridging OH groups existed as shown in Figure 19. Both CO and
formic acid react with the OH groups to generate bidentate formate species. In this mechanism, the cleavage of the formate C-H bond is the rate limiting step. In their subsequent papers dealing with the WGS reaction [90, 91], Davis et al demonstrated that the presence of water is an important factor; the water catalyses the decomposition of surface formates to give CO₂ and H₂. In even later work [92-96], Davis and his group studied the effect of doping alkali metal into the catalysts and found that the formate species were more reactive for the dehydrogenation step. In-situ IR spectroscopy results showed that the electronic properties of formate were changed by introduction of the alkali metal, this leading to a significant weakening of the C-H bond in the formate. Hence, the cleavage of the C-H bond was facilitated by doping alkali metal into the catalysts.

Figure 19: Schematic representation of bidentate formate species produced by both WGS and formic acid decomposition over reduced Pt/thoria; reproduced from reference[89]

In a study of the WGS reaction by Flytzani et al.,[63, 97-99] something new in heterogeneous catalysis was proposed. They found that the metal nanoparticles in Au/CeO₂ or Pt/CeO₂ did not participate in the WGS reaction at low temperatures[97]. They postulated that non-metallic gold or platinum species, adsorbed through an ionic-covalent bond to the CeO₂ support, contribute to the catalytic reactivity. After a series
of experimental and theoretical analyses, Flytzani and her colleagues [98] showed that the presence of alkali metal ions in small amounts promote atomically dispersed Pt on oxide supports for the WGS reaction in the low temperature WGS reaction. In a review of the subject [100], Thomas summarized their work and explained how the alkali metal ion stabilized Pt-OH\textsubscript{x} and that this catalyzes the WGS reaction as shown in Figure 20.

![Figure 20](image)

**Figure 20:** Schematic Pt-OH\textsubscript{x} species stabilized by alkali metal ions for catalysing WGS reaction at low temperature; reproduced from reference [100]

A similar high activity for formic acid decomposition was achieved over supported atomically dispersed gold catalysts [62, 63]; in essence, Ojeda and Iglesia suggested that alumina-supported TEM-invisible sub-nanometre gold species are responsible for the high activity for formic acid decomposition. In contrast, Flytzani et al suggest that the reaction pathway proceeds via a methyl formate (HCOOCH\textsubscript{3}) intermediate which contribute to CO-free hydrogen production without any involvement of the WGS reaction in the mechanism.

All in all, most of the work on formic acid decomposition based on heterogeneous catalysts over the past half century was summarized above. The purpose of this work has changed from investigating catalytic properties of different catalysts using the reaction as a model at the very beginning to recently aiming at high-purity hydrogen
production. Noble metals, Pd, Pt and Au were preferred, these showing both high activities and high hydrogen selectivities. In addition, the exploration was carried out in both vapor and aqueous phases; the highest activity, with a TOF of 7024 h\(^{-1}\) at 473 K was obtained in the vapor phase over an Au/SiO\(_2\) catalyst.

4 The application of Fourier transform infrared (FTIR) spectroscopy in the analysis of catalytic mechanisms

FTIR is a common technique used to obtain an infrared spectrum of adsorption, desorption, emission of a solid, liquid or gas. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is an infrared spectroscopy technique used in this thesis for further understanding the reaction mechanism. Hence, use of infrared spectroscopy in studying formic acid decomposition is reviewed in this section.

4.1 FTIRS related background of formic acid

Formic acid has two geometries, cis and trans; see Figure 21. The trans-form has two hydrogen atoms opposite the CO bond, while the cis-form has two hydrogen atoms on the same side as the CO bond. As a vapor, formic acid exists favorably in the trans-configuration due to its ability to dimerise, some 100 times more likely than for the cis-form at room temperature. It should be noted that the molecule is not dimerised when it is dissociatively adsorbed on a catalyst surface[81]. Because of this, only the trans-form of formic acid is discussed in this section. The nine different vibrational modes of trans-form formic acid are represented in Figure 23 and the corresponding IR band positions are summarized in Table 5. Compared with adsorbed formate, formic acid has two main extra stretching vibrations of the C=O and C-OH bonds while it lacks the essential vibrations (both asymmetric and symmetric) of OCO of a formate species.
Figure 21: Two different geometries of formic acid; reproduced from reference [101]

Table 5: The band positions corresponding to vibration modes of formic acid [102, 103]

<table>
<thead>
<tr>
<th>Mode</th>
<th>Assignment</th>
<th>IR wavenumber, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1)</td>
<td>OH stretch</td>
<td>3570, 3750</td>
</tr>
<tr>
<td>(v_2)</td>
<td>CH stretch</td>
<td>2943, 2942</td>
</tr>
<tr>
<td>(v_3)</td>
<td>C=O stretch</td>
<td>1770, 1777</td>
</tr>
<tr>
<td>(v_4)</td>
<td>CH bend</td>
<td>1387, 1380</td>
</tr>
<tr>
<td>(v_5)</td>
<td>OH bend</td>
<td>1229, 1223</td>
</tr>
<tr>
<td>(v_6)</td>
<td>C-O stretch</td>
<td>1105</td>
</tr>
<tr>
<td>(v_7)</td>
<td>OCO deform</td>
<td>625, 626</td>
</tr>
<tr>
<td>(v_8)</td>
<td>CH bend</td>
<td>1033</td>
</tr>
<tr>
<td>(v_9)</td>
<td>torsion</td>
<td>638, 641</td>
</tr>
</tbody>
</table>
Figure 22: The gas phase infrared spectrum of formic acid; reproduced by National Institute of Standards and Technology (NIST)

Figure 23: vibration modes of formic acid; reproduced from reference[102]
4.2 FTIRS related background of formate

The formate species is widely accepted as an important intermediate during both formic acid decomposition and the water-gas shift reaction. In consequence, there have been many investigations of the adsorption of formate species on catalysts by FTIR spectroscopy. The six modes of vibration of formate on a metal surface in a bidentate bridging adsorption mode are shown in Figure 24. The corresponding IR bands [104] are found at approximately 2824 cm\(^{-1}\), \(\nu(CH)\); 1584 cm\(^{-1}\), \(\nu_{as}(OCO)\); 1352 cm\(^{-1}\), \(\nu_{s}(OCO)\), 776 cm\(^{-1}\), \(\delta(OCO)\), 1384 cm\(^{-1}\), \(\delta(CH)\) and 1072 cm\(^{-1}\), \(\pi(CH)\). Virtually all the bands are slightly shifted by the influence of different catalytic metals, promoters and so on.

![Figure 24: Six possible modes of vibration of bridging formate species on a metal surface; reproduced from reference [104, 105]](image)

4.3 The main band positions over different catalysts

In last two sections, both the vibration modes and band positions of formic acid and formate were discussed generally. However, the band position slightly changes under different conditions. In addition, carbonates as another reaction intermediates have also been reported during the formic acid decomposition under special reaction conditions.
Figure 25 shows the four carbonate adsorption states and Table 6 summarized the main band positions of the possible vibrations involved in formic acid decomposition.

**Table 6:** The summary of main band positions involved in formic acid decomposition over different catalysts

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Ref</th>
<th>Ir/SiO₂</th>
<th>Rh/SiO₂</th>
<th>Ir/Al₂O₃</th>
<th>Pt/ceeria</th>
<th>Au/CeO₂</th>
<th>Au/SiO₂</th>
<th>SiO₂</th>
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<tr>
<td>v(CH) (formic acid)</td>
<td>Ref</td>
<td>[65]</td>
<td>[65]</td>
<td>[65]</td>
<td>[88-90, 106]</td>
<td>[61]</td>
<td>[61]</td>
<td>[51]</td>
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<tr>
<td>2942, 2920</td>
<td>[65]</td>
<td>2942,</td>
<td>2944,</td>
<td>2933,</td>
<td>2917,</td>
<td>2913</td>
<td>2928</td>
<td>2946</td>
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<tr>
<td>v(CH) (formate)</td>
<td></td>
<td>2847</td>
<td>2863</td>
<td>2845,</td>
<td>2945,</td>
<td>2955,</td>
<td>2857</td>
<td>2830</td>
</tr>
<tr>
<td>v(CO) (formic acid)</td>
<td>1722</td>
<td>1723</td>
<td>1714</td>
<td>1728</td>
<td>1733</td>
<td>1725</td>
<td></td>
<td></td>
</tr>
<tr>
<td>v₃(UCO) (formate)</td>
<td>1586</td>
<td>1590</td>
<td>1597</td>
<td>1586</td>
<td>1602</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v(UCO) (formic acid and formate)</td>
<td>1391</td>
<td>1375</td>
<td>1394</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v₃(UCO) (formate)</td>
<td></td>
<td>1580</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v₃(UCO) (formate)</td>
<td>1375,</td>
<td>1300</td>
<td>1316</td>
<td>1361</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v₃(UCO) (carbonate)</td>
<td>1369</td>
<td>1310</td>
<td>1381</td>
<td>1391</td>
<td>1377</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>v₃(UCO) (carbonate)</td>
<td></td>
<td>1460</td>
<td></td>
<td></td>
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<tr>
<td>v₃(UCO) (carbonate)</td>
<td>1350,</td>
<td>1395</td>
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</table>
4.4  Investigations of formic acid decomposition by FTIR spectroscopy

As was discussed above, the introduction of an alkali metal into a catalyst promotes the reactivity for formic acid decomposition and this was explained by alkali ions facilitating the cleavage of CH bond of formate. FTIR results in work from Davis’s group strengthened the reliability of the former explanation[93]. They found that a systematic decrease in the band position of $\nu$(CH) occurs with an increasing atomic number of the alkali metal; see Figure 26. This result implies a weakening of the CH bond. The band at higher wavenumber around 2950 cm$^{-1}$ is ascribed to the coupling of $\nu_s$(OCO) and $\delta$(CH) while the one at lower wavenumber is attributed to $2\delta$(CH). There is clearly a red shift in the band position of $2\delta$(CH) with an increasing atomic number of the alkali metal whereas the band for $\nu_s$(OCO) + $\delta$(CH) is not affected.

---

**Figure 25:** Four carbonate binding modes on noble metals; reproduced from reference[107]
Different adsorption modes of formate on metals also lead to different IR band positions. Tsang et al.[105] prepared several Ru based catalysts with different nanoparticle sizes. As shown in Figure 27, they found in the adsorption mode of bidentate bridging formate, the commonly accepted mode, bands at 1585 and 1362 cm\(^{-1}\) which they attributed to asymmetric and symmetric stretching of OCO, in line with other published data; for the adsorption mode of monodentate formate, they found the corresponding bands at 1618 and 1330 cm\(^{-1}\).

**Figure 26:** The band position of formate v(CH) depended on alkali metals, (a) high alkali doping and (b) low alkali doping; reproduced from reference [93]
**Figure 27:** IR spectra of formate species on different size of Ru nanoparticles: a) 1.8, b) 2.3, c) 2.7, d) 3.2, e) 4.0 nm at room temperature; reproduced from reference[105]

**Figure 28:** Experimental IR vibrational frequency of different types of formate species over oxides (comb 1 stands for $v_{as}(OCO) + \delta(CH)$ and comb 2 stands for $v_{s}(OCO) + \delta(CH)$); reproduced from reference[108]
Most of the time, one of adsorption modes predominates; for example bridging formate could be the main adsorption mode among adsorbed formate. In this case, the researchers explain the bands ascribed to one adsorbent and ignore different adsorption modes. In their work on oxide-supported Au catalysts, Solymosi [61] and his co-workers concluded that the bands at 1555-1600 and 1386-1361 cm$^{-1}$ could be attributed to the asymmetric vibration of formate and the symmetric stretch of formate, respectively. They did not further separate the IR bands into different adsorption modes. In this paper, they found no formate spectra on pure SiO$_2$ indicating that there was no formation of formate species. In contrast, they found the spectra obtained for Al$_2$O$_3$ and CeO$_2$ supports without Au to be very similar to that obtained for formic acid adsorption on supported Rh catalysts. This implies that the formate species can be located on oxide supports such as Al$_2$O$_3$ and CeO$_2$.

IR bands characteristic of carbonate species are sometimes also found during studies of both formic acid decomposition and the water-gas shift reaction. No CH bond exists in adsorbed carbonates but both the asymmetric and symmetric stretching/bending vibrations of OCO still occur and can be found in IR the spectra. Unfortunately, the band positions of $\nu_{as}(OCO)$ and $\nu_{as}(OCO)$ for formate and carbonate are very close and so it is quite difficult to distinguish them on the basis solely of OCO vibrations. Davis et al[93-95] combined the CH and OCO bands together to distinguish formate from carbonate species and found that the band positions of the asymmetric and symmetric vibrations of carbonates OCO are indeed slightly changed compare with those for the formate.
Figure 29: The summary of infrared spectra of adsorbed HCOOH at 298 K (0.5 min) on (a) SiO$_2$; (b) Pd/SiO$_2$; (c) Ca-Pd/SiO$_2$ 1; (d) Ca-Pd/SiO$_2$ 2; (e) Ca/SiO$_2$; reproduced from reference [51]

Cabilla [51] and co-workers reported an FTIR study of the adsorption of formic acid on clean and Ca-promoted Pd/SiO$_2$. Figure 29 compares the adsorption of formic acid on five different catalysts under the same conditions. Figure 29a clearly shows that no formate appears after the introduction of formic acid onto SiO$_2$ as only C=O and C-H stretching of formic acid were found in the spectrum. In contrast, the spectra obtained with the Ca-Pd/SiO$_2$ catalysts contain bands due to asymmetric and symmetric OCO stretching of formate species. At the same time, there was an attenuation of the vibration bands of formic acid over the promoted catalysts, this confirming the dissociation of formic acid on the catalysts.
5 Conclusion

It is quite difficult to overestimate the importance of the role hydrogen energy will play in a future world. As a sustainable and clean form of energy, hydrogen always faces safety issues during storage and transportation, these being the main drawbacks to its utilization. Besides seeking direct solutions to these problems, such as liquefaction of hydrogen or pressurised-gaseous hydrogen, research on liquid chemical carriers of hydrogen is another recent promising development. Formic acid is attractive to many researchers as a potential source of hydrogen produced by catalytic decomposition. Formic acid is considered as to be a totally sustainable energy carrier since it is one of main products of the hydrolysis of biomass and its production does not involve any extra emission of greenhouse gas. Furthermore, there is the possibility of producing formic acid by reducing CO2 in order to make up a cycle for hydrogen storage.

The research on formic acid decomposition goes back to the beginning of the last century, when most of the work carried out was to distinguish catalysts favouring dehydrogenation from those favouring dehydration, the two decomposition directions of formic acid. Since then, both heterogeneous and homogeneous catalysts have been investigated in formic acid decomposition. Formate species are widely accepted as being the most important reaction intermediates in the mechanistic studies. Researchers summarized the volcano curve between catalytic activity and formation heat of corresponding bulk formates during the earlier research time, which can explained well reaction order is different over catalysts with different formation heat of formate. The following research work confirmed that the noble metals, Pd, Pt and Au, are all good catalysts in formic acid decomposition. Work using in situ FTIR spectroscopy confirms that formate intermediates exist during catalysis and shows that the cleavage of CH
bond is the reaction rate determining step. The same formate intermediates combined the research work of formic acid decomposition and water gas shift reaction. It has been reported that the introduction of alkali metal into various catalysts can accelerate the cleavage of the CH bond in the formate intermediates.

Since hydrogen production is the main purpose of the current investigations of formic acid decomposition, the production of high purity hydrogen under mild reaction conditions is the main target in this research area. The most significant results of some recent investigations are summarised in this chapter. The best result until now is a TOF at 353 K of 2010 h\(^{-1}\) in vapour phase reaction over Au based catalysts with the production of CO at a concentration of less than 10 ppm. However, according to our thermodynamic equilibrium calculations, it is not possible to have completely CO-free hydrogen production by formic acid decomposition. There is still a long way to go to achieve practical hydrogen production from the catalytic decomposition of formic acid.
6 Scope and structure of the thesis

The primary objective of this work is to study hydrogen production from vapour phase catalytic decomposition of formic acid. Pd and Pt based catalysts were investigated in the work reported throughout the thesis. Alkali metals, Li, Na, K and Cs, were used to modify Pd based catalysts and the results obtained by such promotion are discussed. A catalytic reaction mechanism is proposed, this being based on characterisation of the catalysts and analysis of DRIFTS results. For Pt based catalysts, the different performances over Pt catalysts supported on carbon nanofibers that were either undoped or doped by nitrogen were compared in formic acid decomposition. The promoted activity over Pt supported CNFs doped by nitrogen was explained by the results of systematic mechanistic investigation.

Chapter 1 reviewed the research background and previous work on catalytic decomposition of formic acid. A description of significance of hydrogen energy was first given. Early and more recent studies of the catalytic decomposition of formic acid were then separately summarised in two sections. Both of the two sections consisted of discussions of catalytic performance and mechanism. The entire literature review focused on heterogeneous catalytic reaction because the whole PhD work in this thesis was based on heterogeneous catalysts. In addition, previous DRIFTS research work related to formic acid decomposition was also reviewed as DRIFTS has been used as an important technique in this thesis to understand the catalytic reaction.

Chapter 2 described the experimental procedures, catalyst preparation, activity test and catalyst characterization methods used in this thesis. It contained the details of all chemicals related to this thesis. Photographs and schematic figures of the set-up and
experimental procedures were shown in this chapter. Calculation methods were also depicted.

Chapter 3 showed a comparison of the activity results over Pd based catalysts both with and without alkali metals. Both 1 wt. % Pd/C and a Pd powder were used as the original catalysts. In addition, 1 wt. % Pt/C was also used for comparison purposes in this chapter. Beside formic acid decomposition, the water-gas shift reaction over modified catalysts was also investigated. The effect of the introduction of water and CO were also studied.

Chapter 4 continued the work of Chapter 3. In this chapter, the reaction mechanism was discussed. Modified catalysts using different preparation methods were compared and discussed. In order to further understand the mechanism, a series of experimental conditions were adopted in this chapter. The observation of the performance during an unstable period of reaction as well as full catalysts characterisation was used to help to formulate a reaction mechanism.

Chapter 5 showed the results of DRIFTS measurement over Pd/SiO2 and potassium doped Pd/SiO2 catalysts. DRIFT spectra of adsorption and desorption of formic acid were shown and discussed in this chapter. The influences of the introduction of water and of CO were also analysed. The explanation for DRIFTS results helps to confirm the reaction mechanism proposed in Chapter 4.

Chapter 6 described the work on Pt supported on CNFs, both undoped and doped by nitrogen. Promotion of the catalytic activity took place in formic acid decomposition over the catalysts doped by nitrogen whereas doping caused a decline in the activity for ethylene hydrogenation. A series of characterizations were carried out to understand the mechanism of promotion.
Chapter 7 gave the conclusions of the entire work in this thesis.
References


Chapter 2

Experimental Procedures

1 Experimental Materials

Information on all the experimental materials used is shown in Table 1.

Table 1: Specification and source of the chemicals and gases

<table>
<thead>
<tr>
<th>Name</th>
<th>Specification</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>98-100%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>1wt.% Pd/C</td>
<td>205672-25G</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>1wt.% Pd/SiO₂</td>
<td>/</td>
<td>Johnson Matthey</td>
</tr>
<tr>
<td>1wt.% Pd/Al₂O₃</td>
<td>/</td>
<td>Johnson Matthey</td>
</tr>
<tr>
<td>1wt.% Pt/C</td>
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<td>Sigma-Aldrich</td>
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<td>Pd powder</td>
<td>99.9%</td>
<td>Alfa Aesar</td>
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<td>K₂CO₃</td>
<td>≥99%, anhydrous</td>
<td>Fluka Analytical</td>
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<td>/</td>
<td>Sigma-Aldrich</td>
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<tr>
<td>Na₂CO₃</td>
<td>99.9%, anhydrous</td>
<td>Fisons</td>
</tr>
<tr>
<td>Cs₂CO₃</td>
<td>99%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>KHC OO</td>
<td>99%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>KBr</td>
<td>/</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Activated Charcoal</td>
<td>100 mesh, powder</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>
Table 1: Specification and source of the chemicals and gases (continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>Specification</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Carbon, Norit</td>
<td>Granular</td>
<td>Lancaster</td>
</tr>
<tr>
<td>Quartz Sand</td>
<td>106-212 µm</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>1vol.%C₂H₄/He</td>
<td>Analysis class</td>
<td>Air Products</td>
</tr>
<tr>
<td>2.5vol.%CO/He</td>
<td>CP grade, &gt;99.999%</td>
<td>BOC</td>
</tr>
<tr>
<td>2vol.%H₂/He</td>
<td>CP grade, &gt;99.999%</td>
<td>BOC</td>
</tr>
<tr>
<td>1vol.%H₂/Ar</td>
<td>/</td>
<td>BOC</td>
</tr>
<tr>
<td>He gas</td>
<td>CP grade, &gt;99.999%</td>
<td>BOC</td>
</tr>
</tbody>
</table>

2  Catalysts preparation and activity tests

2.1 Catalysts preparation

Palladium and Platinum based catalysts were studied in the work reported in this thesis. Catalysts supported on activated carbon were the main research object. Alumina- and silica-supported catalysts were used for comparison. The impregnation method described below was used to modify the commercial supported catalysts and the pure Pd powder with alkali metal salt. A physically mixing method was also used for comparison.

In addition, Pt catalysts supported on nitrogen-doped carbon nano-fibers (CNFs) were prepared by Ismagilov’s group (Boreskov Institute of Catalysis, Novosibirsk, Russia) in a collaborative project.
2.1.1 Catalyst modification by an impregnation method

An incipient wetness impregnation method was used to modify a commercial supported catalyst with alkali metal salts. The preparation procedure used for a 10:1K-Pd/C catalyst is presented as an example below. 0.3535 g K$_2$CO$_3$ was used to prepare 6.0 g of solution with deionised water. 1.5 g of this K$_2$CO$_3$ solution was then dropped into 0.5 g of the 1wt. % Pd/C catalyst; this weight ratio of 3:1 of the solution to the catalyst was adopted for all the activated carbon supported catalysts. (For Pd/Al$_2$O$_3$, the weight ratio of the impregnation solution and catalyst was 1:1; and a ratio of 2:1 was used for Pd/SiO$_2$.) In order to make the solution disperse uniformly in the pores of catalyst, the mixture was then kept in an ultrasonic bath for 4 hours before drying at room temperature overnight; this was followed by oven drying at 393 K for 8 hours. This procedure gave a K-Pd/C catalyst with a weight ratio of 10:1 or a molar ratio of 27:1 of K: Pd. All the other modified catalysts were prepared by the same procedure using the appropriate alkali metal carbonate salt. Table 2 shows the alkali metal compositions of the modified supported catalysts used in this work.

The impregnation method was also used to modify the Pd powder. A 0.1wt.% K$_2$CO$_3$/H$_2$O solution was prepared which contained 1g K$_2$CO$_3$ in 1000 g of solution. Then 0.221 g of this solution was dropped into 0.2 g Pd powder and the mixture was kept in an ultra-sonic bath for 4 hours before drying at room temperature overnight and then at 393 K for 8 hours. A K concentration of 0.0625% in the catalyst precursor was obtained. Other samples with the K concentrations, 0.125%, 0.25%, 0.6%, 1% and 2% were prepared separately.
Table 2: The supported catalysts samples and composition

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Weight ratio of alkali metal to Pd or Pt</th>
<th>Molar ratio of alkali metal to Pd or Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 K-Pd/C</td>
<td>2:1</td>
<td>5.4:1</td>
</tr>
<tr>
<td>5:1 K-Pd/C</td>
<td>5:1</td>
<td>13.6:1</td>
</tr>
<tr>
<td>10:1 K-Pd/C</td>
<td>10:1</td>
<td>27:1</td>
</tr>
<tr>
<td>20:1 K-Pd/C</td>
<td>20:1</td>
<td>54:1</td>
</tr>
<tr>
<td>Li-Pd/C*</td>
<td>1.76:1</td>
<td>27:1</td>
</tr>
<tr>
<td>Na-Pd/C</td>
<td>5.83:1</td>
<td>27:1</td>
</tr>
<tr>
<td>Cs-Pd/C</td>
<td>33.7:1</td>
<td>27:1</td>
</tr>
<tr>
<td>4:1 K-Pd/SiO₂</td>
<td>4:1</td>
<td>10.9:1</td>
</tr>
<tr>
<td>2:1 K-Pd/Al₂O₃</td>
<td>2:1</td>
<td>5.4:1</td>
</tr>
<tr>
<td>10:1 K-Pt/C</td>
<td>10:1</td>
<td>49.9:1</td>
</tr>
<tr>
<td>K/C1**</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>K/C2***</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

*LiHCOO solution was used as impregnation solution by mixing LiOH and HCOOH
** Norit Activated Carbon was adopted to prepare 10 wt.% K/C1
*** Activated Charcoal was adopted to prepare 10 wt.% K/C2

2.1.2 Catalysts modification by physical mixing

10 wt.% K/C obtained by previous procedure was mixed with 1 wt.% Pd/C or 10:1 K-Pd/C in mortar and ground toether. The compositions of the catalyst samples prepared in this work are shown in Table 3.
Table 3: Composition of K and Pd in the physically mixed catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Weight ratio of K to Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/C mix Pd/C (1:1)</td>
<td>10:1</td>
</tr>
<tr>
<td>K/C mix Pd/C (10:1)</td>
<td>100:1</td>
</tr>
<tr>
<td>K/C mix K-Pd/C (1:1)</td>
<td>20:1</td>
</tr>
</tbody>
</table>

2.1.3 The preparation of Pt catalysts supported on nitrogen-doped CNFs

The preparation procedure below was performed by Ismagilov’s group in Russia.

Synthesis of the N-CNFS was carried out in a flow quartz reactor (V=35cm³) with a fluidized catalyst bed at atmospheric pressure. Four different N-CNFS samples (with 0, 1, 3.4 and 7.5 wt.% N) were synthesized by decomposition of a C₂H₄/NH₃ mixture (concentration of NH₃ = 0, 25, 50 and 75 wt.%) over a 65Ni-25Cu-10Al₂O₃ (wt.%) catalyst at 550°C for 1h. The synthesized N-CNFS were treated with concentrated hydrochloric acid to remove the exposed particles of the catalysts used in the synthesis [1-4].

A precipitation method was used to prepare the Pt/N-CNFS catalysts using the starting Pt compound, H₂PtCl₆. This Pt precursor was deposited by NaOH on suspended N-CNFS supports, this being followed by filtration and drying. Three catalysts with different Pt contents were prepared for the work shown in this thesis as follows: 0.3Pt/7.5N-CNFS, 1Pt/0N-CNFS, 1Pt/3.4N-CNFS, 1Pt/7.5N-CNFS, 10Pt/0N-CNFS, 10Pt/3.4N-CNFS, and 10Pt/7.5N-CNFS. All the samples were reduced in a 1 vol. % H₂/Ar mixture at 523 K for 1 h before characterisation measurements.
2.2 Catalytic activity tests

Figure 1 shows the reactor system used for catalytic activity tests. Formic acid decomposition, water gas shift and ethylene hydrogenation were all carried out all carried out using this setup in the work reported in this thesis.

![Diagram of reactor system](image)

**Figure 1:** Scheme of activity test setup system

2.2.1 Formic acid decomposition

For all the catalytic experiments, the catalyst with a certain amount of Pd or Pt (generally containing 0.68/0.068 mg Pd or Pt) was introduced into a quartz tubular reactor of 4 mm internal diameter. All the samples were reduced in a 1 vol. % H₂/Ar mixture at 573 K for 1 h before the reaction and then cooled down in He to the reaction temperature. A mixture of 2 vol. % formic acid in He at a total flow rate of 51 cm³ (STP)
min\(^{-1}\) was introduced into the fixed bed reactor using a syringe pump (Sage). The reactants and products were analyzed by a gas chromatograph (HP-5890) fitted with a Porapak-Q column and a TCD detector [5, 6].

For study of the effects of ethylene hydrogenation and of added CO on formic acid conversion, 1 vol. % ethylene/He and 2.5 vol. % CO/He were used as carrier gas instead of the He.

### 2.2.2 Water gas shift (WGS) reaction

As in the formic acid decomposition experiments, the water gas shift reaction was carried out in the fixed bed reactor. A mixture of 2.5 vol. % CO in He was passed through a water steamer (shown in Figure 1) and this gave 2.3 vol. % H\(_2\)O at 293 K in the mixed gas flow introduced into the reactor.

### 3 Calculation procedures

#### 3.1 Conversion and selectivity

The conversions and selectivity were determined by calculation of the concentrations from the product peaks from the GC. For the formic acid decomposition, there was no other product found other than H\(_2\), CO\(_2\), H\(_2\)O and CO, so it is considered that only two reactions took place during formic acid decomposition in this work:

\[
HCOOH \rightarrow H_2 + CO_2, \]

\[
HCOOH \rightarrow H_2O + CO. \]

Based on this assumption, the reaction conversion was calculated by the equation
\[ Conversion = \frac{[CO + CO_2]}{[CO + CO_2]_{total\ decomposition}}, \]

while the hydrogen selectivity was calculated by the equation

\[ Selectivity = \frac{[CO_2]}{[CO + CO_2]}, \]

where \([CO + CO_2]\) is the sum of volume concentrations of CO and CO\(_2\), and \([CO + CO_2]_{total\ decomposition}\) is the sum of volume concentration of CO and CO\(_2\) when formic acid decomposed totally, the latter also being the initial concentration of reactant formic acid. For the water shift reaction

\[ H_2O + CO \rightarrow H_2 + CO_2, \]

the concentration is simply calculated by the equation

\[ Conversion = \frac{[CO_2]}{2.5}, \]

where 2.5 vol.% is the initial volume concentration of CO.

### 3.2 Turnover frequency (TOF)

The turnover frequency (TOF) of reaction was also calculated to describe the reaction rate over different catalysts. Typically, the TOF is defined as the number of molecules reacted or produced per catalytic active site per unit of time. In this work, all the surface metal atoms exposed to the reactant were assumed to be active sites and so the TOF’s reported in this work are the number of reacted molecules per surface atom of metal per second. On the basis of the assumption that all the catalysts particles seen in TEM
images (see Section 4.1) are ideal spheres, the number of surface atoms was calculated by the steps outlined in the following section.

### 3.2.1 Specific metal surface area, $A_s$

The specific metal surface area $A_s \, (\text{m}^2 \, \text{g}^{-1})$ is determined by the size of the particles of the catalysts determined by electron microscopy as described below in Section. It can be calculated by dividing the average surface area of the particles, $S_p \, (\text{m}^2)$, by the weight of catalyst particles $W_p \, (\text{g})$; $W_p$ is calculated by multiplying the volume of particles $V_p \, (\text{m}^3)$ by the density $\rho_m \, (\text{g} \, \text{m}^{-3})$, these values being determined from the mean particle size $d_p \, (\text{m})$ obtained from TEM images.

$$S_p = \pi d_p^2$$

$$V_p = \frac{\pi d_p^3}{6}$$

$$W_p = V_p \rho_m$$

$$A_s = \frac{S_p}{W_p} = \frac{6}{d_p \rho_m}$$

Alternatively, the specific metal surface area could also be determined from the number of surface metal atoms $N_s$ by multiplying the atomic area $S_a \, (\text{m}^2 \, \text{atom}^{-1})$ by the number of surface metal atoms $N_s$ per metal weight used for the sample $W \, (\text{g})$.

$$A_i = \frac{S_a N_s}{W}$$

Hence, the number of surface metal atoms in the samples is determined by the equation below.
\[ N_s = \frac{6W}{d \rho m S_a} \]

### 3.2.2 Total molecular reaction rate, \( R_t \)

The total molecular reaction rate \( R_t \) (mole s\(^{-1}\)) is the total number of molecules reacted or produced per unit time. It is determined by the reactant flow rate \( V \) (L s\(^{-1}\)), the initial formic acid concentration \( C_{\text{initial}} \) (%) and its conversion (%). The total molecular reaction rate can be calculated by the equation below, where 22.4 is the standard molar volume of an ideal gas (L mol\(^{-1}\)) and \( N_A \) is the Avogadro constant.

\[
R_t = \frac{\text{Conversion} \times V \times C_{\text{initial}} \times N_A}{22.4}
\]

The turnover frequency (TOF) was then calculated by the equation below.

\[
\text{TOF} = \frac{R_t}{N_s} = \frac{\text{Conversion} \times V \times C_{\text{initial}} \times d \rho m S_a}{22.4 \times 6W}
\]

**Table 4: Metal parameters used for TOF calculations**

<table>
<thead>
<tr>
<th></th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic weight, (g mol(^{-1}))</td>
<td>106.4</td>
<td>195.09</td>
</tr>
<tr>
<td>Atomic area ( S_a ), (nm(^2) atom(^{-1}))</td>
<td>0.0787</td>
<td>0.080</td>
</tr>
<tr>
<td>Density ( \rho_m ), (g cm(^{-3}))</td>
<td>12.02</td>
<td>21.45</td>
</tr>
</tbody>
</table>
3.3 Apparent activation energy, $E_a$

The activation energy $E_a$ (kJ mol$^{-1}$) is typically the minimum energy required to start a chemical reaction. The Arrhenius equation below gives a quantitative relationship between the activation energy and the rate constant,

$$k = Ae^{-E_a/RT}$$

where $A$ is the pre-exponential factor, $R$ is universal gas constant. Generally, linear line as plotted by the correlation between $\ln k$ and $1/RT$, where the slope gives the activation energy $E_a$.

$$\ln k = \ln A - \frac{E_a}{RT}$$

4 Characterization of the catalysts

4.1 Transmission electron microscopy (TEM)

Transmission electron microscopy was used to investigate the surface morphology and metal particle sizes of all the catalyst samples used in this work. A JEOL JEM-2100F (80-200 Kv, 0.14 nm resolution) microscope, equipped with a Gatan Ultrascan 1000 digital camera, was adopted for the capture of the surface micro imagines. This instrument includes an EDAX X-ray energy dispersive spectrometer (EDX) and a JEOL high angle annular dark field (HAADF) detector and these were utilized for the analysis of the element location.

Prior to analysis, all the catalysts were reduced at 573 K for 1 hour in a 1 vol. % H$_2$/Ar gas mixture. For the catalysts that had not been doped by alkali metal carbonate, isopropanol was used to disperse the catalysts particles and one drop of the dispersion was added to a carbon film mesh. For the catalysts doped by alkali metal carbonate, a
carbon film mesh was immersed in the catalyst powder; the mesh was covered by a small amount of catalyst and the excess powder was removed by vacuuming. At least 100 metal particles were used to calculate a mean particle size from the images produced by application of Fiji image software.

4.2 X-ray photoelectron spectroscopy (XPS)

For Pd-based catalysts, XPS studies were performed with a Kratos Axis 165 spectrometer using monochromatic Al Kα radiation \( (hν = 1486.58 \text{ eV}) \) and a fixed analyzer pass energy of 20 eV. The binding energy scale was referenced against the C 1s line (284.8 eV). Prior to analysis, all the samples were reduced in 1 vol. % H\(_2\)/Ar gas mixture at 573 K for 1 hour and transferred into the analysis chamber in air.

For Pt-based catalysts, XPS measurements were recorder on an ES-300 photoelectron spectrometer (KRATOS Analytical) with an Al Kα source (Russia). The binding energy of Au-4f\(_{7/2}\) at 84.0 eV was used for the spectra calibration. Special experiments on the determining of the Pt state in the 1Pt/7.5N-CNFs sample before and after reduction in hydrogen were performed at the BESSY II Synchrotron Centre (Berlin).

4.3 BET Surface Area

The specific surface areas of all the catalysts used throughout this work were measured using a Micrometrics Gemini 236 BET analyzer. The technique is based on the isotherm derived by Brunauer, Emmett and Teller (BET) for physical multilayer adsorption onto a surface.

\[
\frac{P}{V(P_0 - P)} = \frac{1}{V_mC} + \frac{C+1}{V_mC} \left( \frac{P}{P_0} \right)
\]
P = equilibrium pressure.

$P_0 =$ saturation pressure of the adsorbate at the measured temperature.

V = corresponding gaseous volume at the pressure P of adsorbed molecules.

$V_m =$ volume V required for a monolayer coverage of adsorbate.

C = constant, related to the enthalpy of adsorption.

During the analysis, N$_2$ was used as the adsorbate and the adsorption process took place at boiling point of N$_2$, 77 K. The range of $\frac{P}{P_0}$ in the equation above used for the BET measurement was 0.05-0.3. Typically, prior to analysis all the samples were dried at 473 K for 2 hours in N$_2$ gas. Around 100 mg amounts were used for the BET measurements of all the samples as most of the samples used in the thesis had high surface area.

### 4.4 X-Ray Diffraction (XRD)

XRD measurements were used for the Pd-based catalysts studied in this work. This analysis was carried out with a Philips X’Pert Pro MPD diffractometer equipped with Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) between the X-ray source angles in the range 10$^\circ$-70$^\circ$. Prior to analysis, all samples were reduced in a 1 vol. % H$_2$/Ar gas mixture at 573 K for 1 hour following cooling down to room temperature in He.

### 4.5 CO Chemisorption

CO chemisorption was performed using a Micromeritics AutoChem 2910. Samples of Pd catalysts were heated in a 5 vol.% H$_2$/N$_2$ mixture at 10 K min$^{-1}$ to 573 K and kept for 1 h at this temperature. Then the sample was held in a flow of N$_2$ at the same
temperature for 1.5 h and cooled to 323 K to perform pulse CO chemisorption. A stoichiometry factor of 1.67 was used[7] for calculation of the dispersion.

4.6 Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)

TOF-SIMS analysis was carried out in a TOF-SIMS 5 instrument (ION-TOF GmbH) using 30 keV Bi\(^{1+}\) primary ions. The target current was 0.11 pA for surface imaging and 0.35 pA for spectrometry.

5 Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

Diffuse reflectance infrared Fourier transform spectroscopy is an infrared spectroscopy technique used for powdered samples. The principle of the operation of DRIFTS is shown in Figure 2. The first scientists to introduce the use of this technique in catalysis were Fuller and Griffiths in 1978.[8] They developed the use of the collection of diffused reflectance using a collector in the shape of a half spheroid. Since then, the technique has been widely used to detect the adsorption and desorption occurring in catalytic reactions and even, in order to understand the catalytic reaction mechanism, to determine the nature of the active reaction sites and the structures of active intermediates. In addition, it is also possible to track, in situ, the process of a reaction under conditions close to those used in a reaction, with different temperatures, pressures and gas atmospheres. Such results give important evidence to provide a further understanding of the catalytic mechanism at a molecular level. In this thesis, the mechanism of the catalytic decomposition of formic acid was investigated using DRIFTS.
Figure 2: The principle of obtaining DRIFT spectra for powder samples; reproduced from reference [8]

5.1 Experimental device

A SpectraTech-0030 DRIFTS “in situ” cell was used, this being fitted with flat ZnSe windows (see Figure 3). A Nicolet Magna 560 FT-IR spectrometer with an MCT detector was used for the DRIFTS measurement. OMNIC IR data software was applied to analysis of the IR data.
Figure 3: A SpectraTech diffuse reflectance infrared Fourier transform (DRIFT) cell: top, viewed from above; bottom, a schematic representation of the cell

5.2 Experimental procedure for DRIFT measurements

A certain amount of catalyst was introduced into the ceramic measurement container in the cell and the surface of the catalyst was slightly pressed to make it flat and flush with the container edge; the amount of the sample used in the DRIFTS measurement
depended on the density of the catalyst. The dome with the ZnSe windows was then put on the cell and screwed tightly with the nuts. The water cooling system was turned on before the cell temperature was increased for any tests. As with the activity experiments in a fixed bed reactor, before use all the catalysts were reduced at 573 K for 1 hour in 1 vol. % H\textsubscript{2}/Ar gas mixture. After reduction, the H\textsubscript{2}/Ar gas mixture was replaced by pure He gas. During the time of cooling down in He gas, single beam scanning was carried out at several temperatures and these spectra were used as background data for the subsequent adsorption measurements at the corresponding temperatures. To investigate the adsorption and desorption of formic acid, a 2 vol.% formic acid/He mixture was introduced into a catalysts sample maintained at 333 K and absorbance spectra were recorded as a function of time, correction being made for the background spectra. Then the gas with formic acid was replaced by pure He and the absorbance spectra were recorded at different temperature up to 493 K.

For the IR spectra measurement of liquid formic acid, a total reflectance foil was also used without the dome to obtain the spectrum. One drop of formic acid was placed on the foil and absorbance scanning was carried out at room temperature, a single beam of clean foil being used as a background.
Reference


Chapter 3

Activity improvement in catalytic hydrogen production by doping alkali metals into Pd/C catalysts

Abstract

A considerable doping effect of alkali metal ions on the activity of a 1 wt.% Pd/C catalyst in hydrogen production from formic acid vapor (2 vol.%) has been observed. The doping effect follows the order K ≥ Cs > Na > Li. With a sample containing 10 wt.% K, the steady-state turn-over frequency at 353 K is found to be 1 s\(^{-1}\), this value being 65 times higher than that for the undoped material. The apparent activation energies for the reaction over the different catalysts were found to increase with doping from 65 kJ mol\(^{-1}\) to 97 kJ mol\(^{-1}\). The content of CO in the products was less than 30 ppm. Experiments on the water-gas shift (WGS) reaction had a similar promotional effect with K-doped Pd/C and Pt/C catalysts; however, methanol decomposition was less influenced by doping K into the catalysts. Both K and Pd involved in a synergetic action in promoted reactions; besides, the formation of formate intermediates is an essential factor to accelerate the reaction rate.
1 Introduction

Although it is well-accepted that hydrogen has significant advantages as a fuel compared with more conventional molecules, there are still problems associated with its production, storage and transportation [1, 2]. One solution for applications such as mobile fuel-cells is to produce the hydrogen in-situ by a reaction such as the steam reforming of methanol. However, this reaction has associated with it the production of CO$_2$, a green-house gas. There would be a significant advantage if the hydrogen could be produced from a biomass-derived molecule since any CO$_2$ formed in parallel would be considered as carbon-neutral or “green”. Hydrogen can be obtained by the gasification of biomass or bio-oil at high temperatures using catalysis[3, 4] but this route is not easily applied to mobile systems. Potentially more valuable as a source of hydrogen is formic acid, a molecule that is formed as a by-product in the acid-catalysed hydrolysis of biomass[5, 6]. Formic acid is easily handled and it can therefore be used for hydrogen storage for transportation applications [7]. It is also worth noting that formic acid can be used directly as a hydrogen donor for hydrogenation and deoxygenation reaction instead of molecular hydrogen [6, 8, 9]. A requirement for the use of formic acid as a hydrogen source is that it would provide stable, CO-free hydrogen generation at low temperatures (<373 K). This demand can be achieved by careful choice of a catalyst and reaction conditions and a significant amount of work on the decomposition of formic acid is currently in progress aimed at finding suitable combinations.

Hydrogen production from formic acid using heterogeneous catalysts has been studied in both the liquid [10-12] and vapour [8, 13-19] phases. For the liquid phase formic acid decomposition, Tedsree et al. [10] have reported that unsupported Pd nanoparticles
show higher initial activities in the decomposition of formic acid in the liquid phase than do nanoparticles of Rh, Pt, Ru, Au and Ag; however, these authors found that a catalyst consisting of Ag nanoparticles covered by a thin layer of Pd had the highest initial activities. For the reaction in the vapour phase, it has been reported that catalysts containing noble metals have better activities than those containing Cu or Ni, these only giving decomposition at higher temperatures (>423 K) [18]. Solymosi et al. [19] found the following trend of activity in vapour phase decomposition of formic acid for carbon supported noble metals:

Ir>Pt>Rh>Pd>Ru.

The previous work in our lab showed that Pd supported on C is an excellent catalyst for formic acid decomposition and the steady-state turnover frequency (TOF) for a 1wt% Pd/C catalyst was about 0.07 s\(^{-1}\) at 373 K [8]. This value was only slightly lower than the value for an Ir/C catalyst (0.096 s\(^{-1}\)) reported by Solymosi et al. [19] for experiments carried out under similar conditions. For the liquid phase formic acid decomposition in the presence of Na formate, Zhou et al. [11] used catalysts based on Pd-Ag and Pd-Au that were doped with ceria and showed that the presence of the formate gave a considerable improvement of the rate of hydrogen production from formic acid; the maximum values of TOFs reported were about 0.06 s\(^{-1}\) at 365 K. Bi et al. [20] and Wang [21] have published results confirming promotion of the reaction by Na formate over Au/ZrO\(_2\) and Pd/C catalysts, respectively. Boddien et al. [22] reported that hydrogen can be generated from alkali metal formates dissolved in water at temperatures less than 373 K when catalysed by homogeneous Ru complexes. With heterogeneous Pd/C catalyst, Wiener et al. [23] has shown the similar performance of decomposition of alkali metal formate at low temperature.
In this chapter, the effects of doping alkali metals, Li, Na, K and Cs, into Pd/C catalysts to promote catalytic activity are reported. The characteristics and catalytic performance of the modified catalysts are investigated. Besides formic acid decomposition, the water-gas shift (WGS) reaction and methanol decomposition are also compared over K-doped Pd/C and undoped Pd/C catalysts. The effect of K on the catalytic activity of Pt/C is also studied. Finally, a possible explanation of the effect of the addition of alkali metal is proposed.

2 Results and discussion

2.1 Characterisation of catalysts

Some of the Pd/C samples doped with alkali metals were characterized by BET surface area, EDS/TEM and CO chemisorption analysis. Figure 1 shows the BET surface areas of the K-Pd/C samples as a function of the amount of K added and also shows the areas of the samples doped by other alkali metal ions with a molar ratio of 27:1. The BET surface area of the undoped sample was 942 m² g⁻¹ and the values obtained decreased with the concentration of the alkali metal ions, the value being as much as 30% lower for the catalyst doped with 20 wt.% K. Comparison of the results for the Li, Na and Cs-doped samples with those for a K content of 10 wt.% (corresponding to the same alkali metal/Pd molar ratio as the other alkali metals) showed that Cs has a stronger effect on the surface area than do Li, K or Na. This is presumably due to the larger size of the Cs ion, its radius being about 2.5 times larger that of the Li ion. It would appear that the alkali metal ions block access to the smaller pores of the carbon support, hence decreasing the apparent surface area. The total pore volume was measured for the Pd/C and 10 wt.% K-Pd/C catalysts and it was found to decrease from 0.49 ml g⁻¹ to 0.33 ml.
g\(^{-1}\); this decrease is in accord with the BET surface area measurements and indicates that the K salt occupies a significant proportion of the volume of the pores.

**Figure 1:** Effect of alkali metal ions on the BET surface area calculated per gram of catalysts

Table 1 summarizes the particle sizes from TEM studies for the K-promoted Pd/C catalysts [13]. The mean Pd particle size of all the samples was about 3.6 nm and this value did not change with K-doping, this indicating that the presence of K species did not bring about any sintering of the Pd crystallites (see Figure 2). Table 1 also shows the results of CO adsorption measurements on the reduced samples. The data show that the CO chemisorption values decrease 1.5 times upon doping with 2 or 10 wt.% K. This indicates that some of the K is probably located on the reduced Pd, partially blocking its surface. The average Pd particle size for the undoped sample was calculated from the CO chemisorption data to be 2.9 nm, a value comparable with that obtained by TEM (~3.6 nm, Table 1). Figure 3 shows the results of line-scanning EDS for the 10 wt.% K-Pd/C catalyst which show that the K ions of this sample were evenly distributed over the entire catalyst surface.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Alkali metal (M⁺) content /wt.% (M⁺: Pd mol ratio)</th>
<th>Dispersion (CO chemisorption(^a))</th>
<th>Mean particle size /nm (TEM)</th>
<th>Activation energy /kJ mol(^{-1})</th>
<th>log(<em>{10})(preexponential factor) /log(</em>{10})(molecule s(^{-1}) gPd(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt% Pd/C</td>
<td>0 (0)</td>
<td>0.38</td>
<td>3.6±1.7</td>
<td>66±1</td>
<td>29.3±0.1</td>
</tr>
<tr>
<td>Li-Pd/C</td>
<td>1.8 (27)</td>
<td>n/a</td>
<td>n/a</td>
<td>88±4</td>
<td>32.7±0.6</td>
</tr>
<tr>
<td>Na-Pd/C</td>
<td>5.6 (27)</td>
<td>n/a</td>
<td>n/a</td>
<td>99±5</td>
<td>35.0±0.3</td>
</tr>
<tr>
<td>2 K-Pd/C</td>
<td>2.0 (5.4)</td>
<td>0.257</td>
<td>3.2± 1.8</td>
<td>98±2</td>
<td>34.5±0.4</td>
</tr>
<tr>
<td>5 K-Pd/C</td>
<td>5.0 (13.5)</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>10 K-Pd/C</td>
<td>10 (27)</td>
<td>0.245</td>
<td>3.7± 1.3</td>
<td>97±3</td>
<td>35.4±0.5</td>
</tr>
<tr>
<td>20 K-Pd/C</td>
<td>20 (54)</td>
<td>n/a</td>
<td>n/a</td>
<td>87±19</td>
<td>33.7±3.0</td>
</tr>
<tr>
<td>Cs-Pd/C</td>
<td>34 (27)</td>
<td>n/a</td>
<td>n/a</td>
<td>92±10</td>
<td>34.5±1.7</td>
</tr>
</tbody>
</table>

\(^a\) stoichiometry factor of 1.67 was taken for calculations[24]
**Figure 2:** TEM images (top) and particle size distribution (bottom) of the catalysts reduced in hydrogen: 1 wt.% Pd/C (left) and 10:1 K-Pd/C (right)

**Figure 3:** Line scanning EDS/TEM of the 10 wt.% K-Pd/C catalyst
2.2 Catalytic activity in formic acid decomposition
2.2.1 Pd/C catalysts doped by alkali metals

Figure 4 shows the steady-state results for the formic acid conversion as a function of reaction temperature for a series of samples of the Pd/C catalyst doped with different concentrations of K. The formic acid was converted almost exclusively to hydrogen and CO₂, with minor quantities of CO and H₂O, and the conversion increased with K content till 10 wt.%, this value corresponding to a K/Pd mole ratio of 27; further increase of the K content up to 20 wt.% led to a slight decrease of the activity. It would therefore appear that 10 wt.% K is approximately the optimum level; while the undoped sample gave a conversion about 50 % with 99.0 % selectivity to hydrogen at 388 K, the sample containing 10 wt.% K gave a conversion of 50 % with 99.8 % selectivity at 340 K, some 48 K lower.

Figure 4: Temperature dependence of conversion in the decomposition of formic acid on the 1 wt.% Pd/C catalyst with different content of K (wt.%)

Figure 5 shows results obtained for samples prepared from the Pd/C material using different alkali metals ions as dopants, the concentration of each corresponding to the
optimum mol ratio of 27 found for potassium. K had the most marked effect on the measured conversions and the results for Cs were very similar. (The results for Cs may be not so reliable due to difficulties in doping with 34 wt.% of Cs, these probably leading to some separate crystals of Cs carbonate on the catalyst particles.) Na and Li were less effective promoters. It is interesting to note that Li formate has a much lower solubility in formic acid or water as compared to K formate [25] and this is in line with the effect of these dopants on the catalytic activity.

**Figure 5:** Temperature dependence of conversion in the decomposition of formic acid on the 1 wt.% Pd/C catalyst with different doped alkali metal

The reaction temperature and hydrogen selectivity for 50% formic acid conversion over these catalysts is shown in Table 2. With the alkali metal doped-Pd/C, the temperature for 50% conversion decreased significantly with increased concentration of K. The selectivities were higher with the catalysts doped with alkali metals than for the undoped catalyst. Furthermore, the hydrogen selectivities determined experimentally were also higher than those calculated assuming equilibrium of the WGS reaction. For example, the calculated hydrogen selectivity corresponding to equilibrium at 385 K is
98.1% while a value 98.9% was measured experimentally with the undoped Pd/C indicating the reaction rate of reverse WGS is lower than that of formic acid decomposition at low temperature. The CO$_2$ is the primary product and Pd/C catalysts doped with alkali metal are thus selective for dehydrogenation.

**Table 2:** Temperature and selectivity at 50% conversion over all catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Temperature at 50% conversion, K</th>
<th>Selectivity at 50% conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt.% Pd/C</td>
<td>385</td>
<td>98.9%</td>
</tr>
<tr>
<td>Li-Pd/C</td>
<td>374</td>
<td>99.5%</td>
</tr>
<tr>
<td>Na-Pd/C</td>
<td>355</td>
<td>99.8%</td>
</tr>
<tr>
<td>2 K-Pd/C</td>
<td>367</td>
<td>99.6%</td>
</tr>
<tr>
<td>5 K-Pd/C</td>
<td>347</td>
<td>99.8%</td>
</tr>
<tr>
<td>10 K-Pd/C</td>
<td>340</td>
<td>99.8%</td>
</tr>
<tr>
<td>20 K-Pd/C</td>
<td>342</td>
<td>99.8%</td>
</tr>
<tr>
<td>Cs-Pd/C</td>
<td>344</td>
<td>99.9%</td>
</tr>
</tbody>
</table>

All the alkali metal species gave promotion of the Pd/C catalyst, the order of the activity measured for samples with the same metal ion to Pd ratios being $K \geq Cs > Na > Li >$ undoped (Figure 5). Thus, it appears that the cations with the largest radii have the strongest effect on the catalytic activity. As was mentioned above, the solubility of Li formate is lower than the solubility of K formate in formic acid or in water [25]. There is clearly an optimum concentration of alkali metal in the catalyst (Figure 1) which can be related to a limited solubility of alkali metals formates in the liquid condensed in the
poles of the catalysts. Hence, a correlation between a solubility of an alkali metal formate and activity in formic acid decomposition may exist.

### 2.2.2 Activated carbon supports doped by potassium (K/C) without noble metal

In order to check whether the K-doped carbon might be catalytically active without the addition of a noble-metal component, the activities of two different K-doped carbon samples were examined and the results are shown in Figure 6. The conversion of the K-doped carbons (K/C) was negligible at temperatures 348-373 K. Under the same conditions, the conversion of formic acid over the K-doped Pd/C sample was complete (Figures 4 and 5). The K/C materials gave 25% conversion with selectivity of less than 55% at 523 K, this temperature being some 190 K higher than that using the Pd catalyst with 10 wt.% K. Hence, a very significant synergetic effect was attained upon K addition to the noble metal catalysts supported on carbon. This effect must be explained either by joint participation of the K/C and Pd sites in the reaction steps and/or by the decoration of the Pd surface by K.
**Figure 6:** Conversion (a) and H₂ selectivity (b) in the formic acid decomposition over the 10 wt.% K/C (Norit, S_{BET}=580 m² g⁻¹) and 10 wt.% K/C (Darko, S_{BET}=534 m² g⁻¹) samples. Sample weight - 0.068 g

### 2.2.3 Pt/C catalyst doped by potassium

In addition, a Pt/C catalyst was also modified by doping potassium. Figure 7 demonstrates comparable results for the K-doped Pt/C catalyst to those reported above for the Pd/C catalysts, showing that there were similar effects for this material. The undoped Pt/C catalyst was less active than the undoped Pd/C catalyst and the K-doped Pt/C sample was less active than the corresponding Pd/C sample; however, the promotional effect was significant. It is therefore clear that the synergetic effect also takes place in the K-doped Pt/C catalyst.
Figure 7: Promoted activity of Pt/C and Pd/C after doping K in the decomposition of formic acid

2.2.4 Stability test of 10 K-Pd/C catalyst

A stability test of the 10 wt.% K-doped Pd/C catalyst was carried out in an experiment lasting for 22 h at 343 K (Figure 8). The initial conversion was about 66% and the value changed only slightly during the 22 h test to reach about 64%. The hydrogen selectivity remained above 99.8% during this experiment, this corresponding to a CO content of less than 30 ppm.
2.2.5 Arrhenius plots

The concentrations of the surface Pd sites and dispersion of Pd for the K-doped and undoped samples were calculated on the basis of CO chemisorption measurements and the results are given in Table 1. Using the numbers of surface Pd sites, the TOFs for the formic acid decomposition were calculated for each sample and the results are plotted as log (TOF) versus reciprocal temperature in Figure 9. The TOF value at 353 K for the undoped Pd/C catalyst was equal to 0.015 s⁻¹. Doping of the Pd/C catalyst with 10 wt.% K led to a considerable increase of the TOF by a factor of up to 65, giving a TOF equal to 1 s⁻¹.
There is a very significant difference between the apparent activation energies obtained for the K-doped sample and that for the undoped sample: the activation energy for the undoped catalyst was 65 kJ mol\(^{-1}\) while the values obtained for the samples doped with 2 and 10 wt.% K were both 97 kJ mol\(^{-1}\). Considerably increased activation energies were also observed in the case of doping with the other alkali metal ions; the values were in the range 92-99 kJ mol\(^{-1}\) for the samples doped with Na, K and Cs and this should be compared with a value of 88 kJ mol\(^{-1}\) for the Li doped catalyst (Table 1). These increases in the activation energy were compensated by very remarkable increases in the apparent pre-exponential factors (3.4-6.3 orders of magnitude). This increase in the pre-exponential factor on doping with K seems to be related to the amount of K added to the catalyst. In other words, the activation energy increased on the addition of even a small amount of K (2 wt.%) to give approximately the same value as that for the 10 wt.% K sample; however, the value of pre-exponential was significantly lower for the lower quantity of K. This seems to indicate that the nature of
the active sites is the same on all the promoted catalysts but the pre-exponential factor increases with the K content. Despite this change, there was no significant change in the concentration of the surface Pd sites as determined by CO chemisorption or of the Pd particle mean size determined by TEM (Table 1). Hence, we conclude that the rate of the reaction is not only determined by the Pd sites on the catalyst but is related to the number of K sites or to the number of anions corresponding to these sites.

2.3 Effect of K ions on catalytic properties in water-gas shift reaction and methanol decomposition

The undoped and 10 wt.% K-doped Pd/C, Pt/C catalysts were also tested for their activity in the WGS reaction and the results are shown in Figure 10. Both the undoped Pd/C and Pt/C catalysts had almost negligible activity for this reaction at temperatures lower than 573 K. However, the addition of K ions gave a very remarkable increase (by a factor of more than 40) in the activity, the sample containing 10 wt.% K giving reaction at a temperature as low as about 433 K.

![Figure 10: Conversion of CO in the water-gas shift reaction on the 1 wt.% Pd/C and 1 wt.% Pt/C catalysts with and without addition of 10 wt.% of K](image-url)
The undoped and 10 wt.% K-Pd/C samples were also tested for the decomposition of methanol (Figure 11). The conversion was measurable for both these samples, the reaction occurring above about 433 K; the products of the reaction were CO and H₂. The effect of K-doping was much lower than that observed for formic acid decomposition and the WGS reaction, the activity of the catalyst for the reaction increasing only by factor of 2.5. The value of the activation energy did not change upon doping and was about 70 kJ mol⁻¹ (see Table 3). This value was close to that reported by Matsumura et al. [26] for Pd/ZrO₂ catalysts (77 kJ mol⁻¹). These data appear to indicate that the decomposition of methanol takes place mainly on the Pd surface and that K species have very small effect on the rate of reaction.

![Figure 11: Conversion in the methanol decomposition on the 1 wt.% Pd/C catalyst with and without addition of 10 wt.% of K, CH₃OH-2.1 vol.%](image)

In summary, formic acid decomposition and the WGS reaction gave hydrogen on the K-doped catalysts with the rates that were very significantly higher than those over the undoped materials; the effect was very much lower with methanol decomposition. The activity for the formic acid decomposition and the WGS reaction was increased by K-doping by a factor of 10-100 while that for methanol decomposition was only increased.
by a factor of 2.5. Formic acid decomposed to give hydrogen on the K-doped Pd catalyst at temperatures that were about 170 K lower than those for the other two reactions.

**Table 3:** Activation energies for the different reactions (kJ mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Formic acid decomposition</th>
<th>Water-gas shift reaction</th>
<th>Methanol decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt.% Pd/C</td>
<td>65</td>
<td>-</td>
<td>69</td>
</tr>
<tr>
<td>2:1 K-Pd/C</td>
<td>97</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10:1 K-Pd/C</td>
<td>97</td>
<td>66</td>
<td>71</td>
</tr>
<tr>
<td>10:1 K-Pt/C</td>
<td>97</td>
<td>74</td>
<td>-</td>
</tr>
</tbody>
</table>

### 2.4 Explanation of the catalytic promotion

For the formic acid decomposition, the following features of the results reported above are important in gaining an understanding of the mechanism of the promoting effect of alkali metals (taking K as example here): (i) no effect of the K on the Pd particle size (excluding that the effect of K changes the dispersion of Pd); (ii) the strong synergetic effect between the K and Pd; (iii) the high K/Pd atomic ratios, from 5 to 27, necessary to bring about the effect; (iv) the very different values of Ea for the K-doped and the undoped catalysts; (v) the lack of dependence of the value of Ea on the content of K in the range 2-10 wt.% despite a steady increase in the rate of reaction in proportion to the K content; and (vi) the remarkable improvement in both formic acid decomposition and WGS whereas little increase in methanol decomposition. Based on all of above, it is suggested that an essential step is that potassium formate and/or bicarbonate species are formed at the K-doped support as reaction intermediates which then react at the Pd
surface. Adsorbed formate species are widely accepted as reaction intermediates in both formic acid decomposition and WGS but not in methanol decomposition. Fuller discussions of this proposed mechanism, together with further supporting experimental results, are given in subsequent chapters.

3 Conclusions

All the Pd/C catalysts doped by alkali metals gave rise to the production of hydrogen from formic acid decomposition with increased hydrogen selectivity, the rates being very significantly higher than those over the undoped materials and the doping effect order being K≥Cs>Na>Li. The doped catalyst with optimal 10 wt.% K showed the best performance in this work; the reaction rate increased by 2 orders of magnitude and the conversion was almost complete below 373 K. Both the conversion and the hydrogen selectivity remained stable over a period of 22 hours with the 10 K-Pd/C catalyst. EDS/TEM images showed that potassium was evenly dispersed over the entire Pd/C catalyst surface and that the introduction of K did not change the dispersion of the Pd in the catalyst. The significant changes in the activation energy and the pre-exponential factor observed implied that there is a different reaction mechanism in the alkali-metal doped catalysts and the undoped catalysts. The negligible activity found with K/C without added noble metals implied that there is a synergetic effect between Pd and K, this giving much increased catalytic activity. A similar promotion effect was found over Pt/C catalysts doped by K. A remarkable improvement in the WGS reaction was also obtained with the K doped catalysts whereas very little promotion was observed in methanol decomposition. This indicates that the formic acid decomposition and the WGS reaction have similar reaction intermediates, probably a formate, and this could be
the essential factor giving activity promotion. Further discussion of the reaction mechanism is to be found in the following chapters.
References


Chapter 4

A mechanistic study of the production of high purity hydrogen from formic acid on Pd catalysts doped with potassium ions

Abstract

The unsteady state during the early stages of formic acid decomposition over a range of K-doped Pd/C catalysts was investigated in order to gain an understanding of the remarkable improvement in activity due to the presence of potassium. The existence of mobile formate ions in liquid phase of HCOOH in this reaction system was proposed. It was also found that the dispersion of K in a physically mixed K-Pd/C catalyst changed after reduction/reaction, this implying the existence of mobile K and formate ions in this mixture as well. Experiments with an unsupported Pd powder showed that K ions had a similar but smaller promotional effect (<10 times) in this case. It is suggested that during the reaction, formate ions are formed from the K carbonate to give a formic acid/water solution condensed in the pores of the catalysts. The conversion of these formate ions in the presence of water then provides an alternative reaction route, this giving the observed considerably improved rate of hydrogen generation with the K-doped Pd samples.


1 Introduction

It has been found that the catalytic activities in formic acid decomposition of Pd/C catalysts doped by alkali metal are remarkably improved compared with the undoped Pd/C, giving with the steady-state turnover frequency (TOF) of 1 s\(^{-1}\) at 353 K for a 10 wt.% K-Pd/C catalyst [1] (Chapter 3). No published result for catalytic reaction in the vapour phase has been found to have a higher value at the same low temperature. This work was stimulated by the reports that alkali metals have a strong promotional effect on the water-gas shift (WGS) reaction [2-5], the mechanism of which could be related to formic acid decomposition [6, 7]. The results showed that the temperature required for formic acid decomposition could be decreased to <353 K, the rate of hydrogen production being increased considerably (by 1-2 orders of magnitude) by doping with K ions.

In Chapter 3, it is showed that the K doping did not change the dispersion or particle size of the Pd and that the catalyst supports doped by K without noble metal had negligible catalytic activity. Thus, it was speculated that there is a synergetic effect between the Pd and K giving the significant promotion in formic acid decomposition. This chapter gives more detail on the effect of K ions on the catalytic activity of the Pd/C catalyst for formic acid decomposition. Particular attention is paid to the initial stages of the reaction over the catalyst, the results showing that formic acid reacts with K species on both the C and Pd surfaces; formate ions dissolved in an aqueous formic acid solution condensed in the pores of the catalyst appear to participate in the decomposition reaction. K-doped Pd/C catalysts prepared by different preparation procedures have also been investigated. Finally, experiments with unsupported Pd powder doped with K species have been performed to elucidate the role of the potassium on the Pd surface.
2 Results

2.1 Characterisation of Pd catalysts

The basic properties of K-doped Pd/C such as particle size and BET surface area were reported in Chapter 3. This chapter gives extra characterisation work (BET surface area, HAADF/STEM, XRD, XPS, TOF-SIMS) carried out to further study the samples of Pd/C and Pd powder doped with K ions. According to the BET surface area measurement (20 m$^2$ g$^{-1}$) of the Pd powder, an average particle size of 25 nm was obtained, this value assuming a spherical shape for all the Pd particles. With this small surface area, a lower concentration of K (0.0625 wt.% - 2 wt.% K/Pd powder) was chosen to modify the Pd powder for comparison with with the Pd/C sample (BET surface area, 933 m$^2$ g$^{-1}$).

![Figure 1: Line scanning HAADF/STEM measurements of the physically mixed 1 wt.% Pd/C and 10 wt.% K/C (Norit) samples before reaction and reduction (Pd is seen better in the TEM picture)](image_url)
A physical mixture of Pd/C and K/C was prepared by grinding them together in a mortar. This chapter reports activity tests and HAADF/STEM measurements. The HAADF/STEM results indicated that K was absent from the Pd/C component after physical mixing but before the reaction/reduction whereas it was present after reduction and reaction. This implies that the K was mobile during the procedure of reduction/reaction.

![Figure 2: Line scanning HAADF/STEM of the physically mixed 1 wt.% Pd/C and 10 wt.% K/C (Norit) samples after reaction and reduction](image)

XRD measurements (Figure 3) gave a very broad diffraction line corresponding to Pd(111) at $2\theta \approx 40$ degrees, this confirming the high dispersion of the Pd (Pd/C, 3.6 nm; 2 K-Pd/C, 3.2 nm; 10 K-Pd/C, 3.7 nm, reproduced from Chapter 3). Diffraction peaks due to the presence of potassium bicarbonate crystallites were observed for the 10 wt.% K-Pd/C catalyst but these were not observed for the 2 wt.% K-Pd/C sample; this does
not however exclude the possibility that highly dispersed and hence X-ray amorphous potassium bicarbonate also exists in the samples with lower K loadings.

![XRD pattern of the Pd/C catalysts with 2 and 10 wt.% of K and without K](image)

**Figure 3:** XRD pattern of the Pd/C catalysts with 2 and 10 wt.% of K and without K after reduction

The results of TOF-SIMS analysis (positive ion image) for the 10 wt.% K-Pd/C catalyst (Figure 4) showed that K$^+$ ions were produced from the whole sample, this confirming the high dispersion of the K species. K$_2$CO$_3$K$^+$ ions, probably originating from bicarbonate or carbonate species [8], were also emitted, mainly from those parts of the sample containing large particles (2-7 µm) of these compounds. Negative ion TOF-SIMS analysis (not shown) confirmed the presence of HCO$_3^-$ and HCO$_2^-$ ions (formed from bicarbonate species) on the catalyst surface.
Figure 4: Surface image of (a) K and (b) K$_2$CO$_3$K$^+$ ions evolved from the area of 103x103 $\mu$m$^2$ of the 10 wt.% K–Pd/C catalyst obtained by TOF-SIMS analysis. (Bright field indicates the presence of ions)

XPS examination of the samples was carried out to show whether or not there was any significant interaction between the Pd and the K species and the results for the Pd/C and Pd powder samples are summarised in Table 1. The results show that there was no shift in the binding energies of the Pd in either the oxidised or metallic forms when the K content was increased. The results also show that the ratio of the surface concentration of the oxidised form of Pd to the total concentration of Pd did not change noticeably with the addition of K. This does not exclude the possibility that K ions are located on Pd nanoparticles present in the form of islands or at the interface between the Pd and the support in a similar way to that proposed earlier by Mallinson for a Na-Pt/TiO$_2$ system[2]. However, that the main part of surface Pd is present in an undoped state is seen in this case by XPS and there was no evidence from the XPS results for a strong interaction between the Pd and K.
Table 1: XPS data for the Pd/C catalysts and Pd powder

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>K⁺ atomic surface concentration*, at.%</th>
<th>Pd⁰ 3dₓᵧ₂ BE, eV</th>
<th>Pd²⁺ 3dₓᵧ₂ BE, eV</th>
<th>Pd²⁺/(Pd²⁺+Pd⁰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>0</td>
<td>335.7</td>
<td>337.6</td>
<td>0.61</td>
</tr>
<tr>
<td>2 K-Pd/C</td>
<td>0.69</td>
<td>335.6</td>
<td>337.3</td>
<td>0.72</td>
</tr>
<tr>
<td>10 K-Pd/C</td>
<td>3.17</td>
<td>335.6</td>
<td>337.7</td>
<td>0.68</td>
</tr>
<tr>
<td>Li-Pd/C</td>
<td>0</td>
<td>335.7</td>
<td>336.9</td>
<td>0.80</td>
</tr>
<tr>
<td>Pd powder</td>
<td>0</td>
<td>335.4</td>
<td>336.2</td>
<td>0.5</td>
</tr>
<tr>
<td>0.6 wt.% K on Pd powder</td>
<td>6</td>
<td>335.2</td>
<td>336.2</td>
<td>0.67</td>
</tr>
<tr>
<td>2 wt.% K on Pd powder</td>
<td>10</td>
<td>335.2</td>
<td>336.2</td>
<td>0.66</td>
</tr>
</tbody>
</table>

* K⁺ atomic surface concentration = \([K^+]_{on \ surface} / [all \ element \ atoms]_{on \ surface}\), at.%

It is also useful that for the Pd powder the surface K concentration increases only insignificantly with an increase of the K content in the 0.6 and 2 wt.% samples. This may indicate that at the concentration of K of 0.6 wt.% all the surface Pd sites that can be covered by K are already covered. The subsequent increase of K content leads to three-dimensional growth of the K carbonate crystallites.

2.2 Unsteady state over K-doped Pd/C catalyst

Figure 5 shows the results obtained during the first hour of operation for the decomposition of formic acid with the 10 wt.% K-Pd/C sample. Three specific features can be seen, these being typical of the results for all the K-doped samples examined. These are: (i) a greater rate of CO₂ evolution as compared to that of H₂; (ii) a greater
consumption of formic acid by the sample compared to the amounts of products formed from formic acid decomposition; and (iii) a decrease of the rate of formation of CO\textsubscript{2} and H\textsubscript{2} with time. The volume concentration of products H\textsubscript{2} and CO\textsubscript{2} might be expected to be the same, this according to the stoichiometry of formic acid decomposition reaction (1):

\[
HCOOH \rightarrow H_2 + CO_2
\]  

(1)

It is therefore likely that other reactions are taking place after the introduction of HCOOH into the K-doped catalysts. Figure 6 shows the difference between the CO\textsubscript{2} and H\textsubscript{2} concentrations as a function of time for experiments with Pd/C samples doped with different concentrations of K ions. It can be seen that the excess of CO\textsubscript{2} increases with an increase of the K content of the samples. The changes occurring during the early stages of the reaction must therefore be associated with surface reactions that involve the K ions. Hence, it is assumed that the besides the formic acid decomposition reaction (1), the following reaction (2) also takes place after introducing HCOOH onto K-doped catalysts. This equation is based on the assumption that the K ions initially exist on the catalyst in the form of carbonate ions and that they are converted in the early stage of reaction to formate species.

\[
K_2CO_3 + 2HCOOH \rightarrow 2KHCOO + H_2O + CO_2
\]  

(2)
Figure 5: Transient evolution of H$_2$, CO$_2$ and formic acid after a switch of a He flow to a formic acid/He flow over the reduced 10 K-Pd/C sample (0.075 g) at 333 K.

It is therefore considered that the excess of CO$_2$ observed occurs as the product from reaction (2); the amount can be quantified by integration of the curve (CO$_2$ - H$_2$). Table 2 gives the magnitude of these changes expressed as (CO$_2$ - H$_2$) evolved during the attainment of steady-state conditions as a function of the K contents of the samples and also gives the ratio between these values and the K contents. The values of the ratio (CO$_2$ - H$_2$)/K are close to 0.5 and this corresponds to the stoichiometry of reaction (2). In agreement with this suggestion, of the reaction of formic acid with a 10 wt.% K/C sample without Pd gave only CO$_2$ without any H$_2$ in the gas phase and the reaction ceased after about 20 minutes.
Figure 6: Difference between CO$_2$ and H$_2$ concentrations obtained after introduction of formic acid to the 1 wt.% Pd/C catalyst with different content of K ions at 333 K

There was also evidence that a significant proportion of the formic acid consumed in the early stages of the reaction was taken up in the pores of the catalyst without reaction. Figure 7 shows the percentage of adsorbed formic acid (determined as the difference between the quantities of formic acid reduced in total and the amount reacting to give CO$_2$ by either the decomposition reaction or by Eq. 2 discussed above) as a function of the operation time for some of the Pd/C samples, these results indicating that significant molecular adsorption of formic acid occurred on the samples. The amount of adsorbed formic acid determined from the area under the curves also increases with K content; see Table 2, where the amount of adsorbed formic acid is related to the catalyst weight.
Table 2: The difference of the amounts of CO$_2$ and H$_2$ evolved during interaction of formic acid with catalysts at 333 K and the steady-state concentration of adsorbed formic acid

<table>
<thead>
<tr>
<th>K content, wt.%</th>
<th>0</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$-H$_2$, mmol</td>
<td>0</td>
<td>0.075</td>
<td>0.235</td>
</tr>
<tr>
<td>(CO$_2$-H$_2$)/K, mol/mol</td>
<td>0</td>
<td>0.43</td>
<td>0.67</td>
</tr>
<tr>
<td>Adsorbed formic acid weight/ catalyst weight, g/g</td>
<td>0.19</td>
<td>0.31</td>
<td>0.60</td>
</tr>
</tbody>
</table>

For the decrease of the rate of formation of CO$_2$ and H$_2$ with time, it has previously been explained [9] that the decrease of the conversion in time in the early stages of the reaction might be due to the slow accumulation of adsorbed CO on the Pd surface, this inhibiting the decomposition reaction. (CO is formed with a very low selectivity (<0.5%) as a result of the dehydration reaction for the samples doped with alkali ions (Table 2 in Chapter 3)). Inhibition by CO may also contribute to the dynamic behaviour shown in Figure 5 since it is found that the introduction of CO into the reaction mixture brought about a strong inhibition of formic acid decomposition (Figure 8) in the same way that was observed previously for the undoped sample.
In summary, there is a period before the reaction system obtains a steady state when adsorption and other mixed processes take place. A significant fraction of the introduced HCOOH are adsorbed and also condensed in the pores of catalyst and the amount increases with the increasing K concentration. A certain fraction of this
HCOOH decomposes into H₂ and CO₂ and the decomposition rate decreases with time, possibly due to the Pd being poisoned by a small amount of product CO. Besides, another proportion of HCOOH was reacted with doped K carbonate to emit CO₂ which was exhibited as the excess amount compared with that of H₂.

### 2.3 Comparison of the catalytic activity of physically mixed and separate beds of Pd/C and K/C catalysts

Figure 9 compares the catalytic data for formic acid conversion obtained with: (a) the Pd/C catalyst doped by 10 wt.% K deposited by impregnation; (b) a sample of the Pd/C catalyst physically mixed, using a pestle and mortar, with a sample of the 10 wt.% K/C (Norit) sample; (c) the Pd/C sample separated from the 10 wt.% K/C (Norit) sample by a quartz wool plug placed in the reactor with the Pd/C sample on top; and (d) with the samples as in (c) but with the order of the K/C and Pd/C samples reversed (K/C on top). In each of these cases, the same weight of Pd (0.068 mg) was placed in the reactor. It can be seen that the conversion on the physically mixed sample was only slightly lower than that of the K-doped Pd/C sample. However, the conversion using the separated Pd/C and K/C samples was much lower, this being independent of their order in the reactor. Hence, the K had a significant effect only when it was close to the Pd sites. However, without intimate mixing, the K has no effect; this is in accordance with the catalytic tests of the K/C samples without added Pd (Chapter 3) showing that K supported by itself on C had negligible activity at temperatures lower than 373 K. The experiments shown in Figure 9 therefore indicate that the K must be located in the proximity of the Pd in order that the synergetic effect between the K/C and Pd sites occurs. Potassium ions may diffuse to the proximity of the Pd particles in the mixed sample during the reduction in H₂ at 573 K or during the reaction with formic acid. This
was confirmed by the results of an EDS/TEM study (Figures 1 and 2). These results indicate that K was absent from the Pd/C part of the physical mixture before the reaction/reduction but that it was present after reduction and reaction. It appears that such diffusion does not occur through the quartz wool interface, this preventing direct contact of the Pd/C and K/C samples.

![Conversion vs Temperature](image)

**Figure 9**: Conversion of formic acid on (a) the 1 wt.% Pd/C catalyst doped with 10 wt.% of K (7.5 mg); (b) a physical mixture of the 1 wt.% Pd/C catalyst (6.8 mg) with the 10 wt.% K/C (Norit) sample (6.8 mg); (c) the 1 wt.% Pd/C catalyst (6.8 mg) placed on top of the 10 wt.% K/C (Norit) sample (6.8 mg), separated by a quartz wool plug; and (d) same as (c) but in reverse order (K/C sample first)

### 2.4 Catalytic activity over K-doped Pd powder

A series of experiments was carried out using K-doped unsupported Pd powder with different loadings of potassium ions. Figure 10 shows the conversion as a function of the K content for the reaction at 353 K. It can be seen that the conversion increased by a
factor of up to 6 times compared with the undoped sample with increasing K concentrations up to about 0.3 wt.% but that the conversion then reached a plateau value with further addition of K.

**Figure 10:** Effect of K doping on the conversion of formic acid in the decomposition over the Pd powder (6.8 mg) at 353 K

Arrhenius plots of the TOF values calculated from the conversion data for the undoped and some K-doped Pd powders are shown in Figure 11. For the undoped Pd powder, the TOF value was equal to 0.013 s\(^{-1}\) at 353 K and the apparent activation energy was 60 kJ mol\(^{-1}\). The activity increased significantly with K doping and the activation energy increased to 100-108 kJ mol\(^{-1}\) (Figure 11). It is therefore probable that a change of the mechanism for the Pd powder has taken place as a result of K doping.
Discussion

It appears that if the catalyst is modified by K species, the kinetics of the formic acid decomposition reaction is completely changed, implying that the reaction is now occurring in a different way to that which applied on the unpromoted material. A possible reaction mechanism is presented in Figure 12. It contains three main reaction steps: (i) the first reaction step between HCOOH and carbonates takes place at the very beginning of introducing HCOOH into K-doped catalysts (see Eq. 2 above) and formate species, CO$_2$ and water are generated, this step being complete at a temperature lower than 333 K; (ii) in the presence of water (a very small amount is sufficient), the mobile formate ions existing in the condensed/liquid HCOOH adsorbed on the catalysts emits H$_2$ due to reaction at Pd sites (Eq. 3); (iii) the bicarbonate produced from the former step reacts with HCOOH to form formate ions again to complete the reaction cycle (Eq. 4).
Both first step (Eq. 2) and last step (Eq. 4) can take place easily under mild reaction conditions. In the proposed reaction mechanism, the second reaction step (Eq. 3) is rate determining and the existence of liquid/condensed phase is one of the essential factors giving acceleration of this step. It has been shown above that a significant fraction of the formic acid is probably adsorbed/condensed in the pores of the catalysts in the early stages of reaction after introducing HCOOH to the samples. It has been reported that condensed formic acid is observed by infrared spectroscopy on undoped SiO$_2$ [10], and SiO$_2$ doped with K [11] or Ca [10] and with noble metal particles (Au, Ir, Rh, Pd and Cu) supported on SiO$_2$ [10-13]. In all these cases, the IR results showed the presence of a stretching vibration of a hydrogen-bonded carbonyl group (C=O) at a wavenumber of 1715-1735 cm$^{-1}$, this being slightly shifted with respect to the corresponding band for gaseous formic acid and confirming the existence of a condensed phase of formic acid.

![Figure 12: Possible mechanism of formic acid decomposition over K doped Pd catalysts](image)
Hu et al., on the basis of DFT calculations [14] and experimental studies [15], suggested that the mechanism of formic acid decomposition on noble metals in the vapour and aqueous phases is different. They suggested that this difference is due to the presence of formate ions in the aqueous-phase. Most of best results for hydrogen production from the decomposition of formic acid have been obtained with homogeneous catalysts based on complexes of Rh (TOF, 0.6 s\(^{-1}\) at 298 K) [16], Ru (TOF, 1 s\(^{-1}\) at 323 K) [17, 18], Fe (TOF, 2.6 s\(^{-1}\) at 353 K) [19] or Ir (TOF, 3.9 s\(^{-1}\) at 363 K) [20]. The highest activities, with TOF value of 1 s\(^{-1}\) at 353 K and excellent hydrogen selectivity (>99.8%), obtained in this work are comparable to those for the decomposition of aqueous formic acid solutions using homogeneous catalysts. It should be noticed that experiments on formic acid decomposition in the liquid phase have most often been performed in the presence of water, different amines or formates, all of which promote the reaction activity. The concentration of formate ions in formic acid on its own is very small as the latter is a weak acid, its dissociation constant being only 1.7x10\(^{-4}\). In contrast, alkali metal formates are completely dissociated in formate solutions. Hence, the formate ion concentration in the K formate solution in the pores of the catalysts is several orders of magnitude greater than if no K formate is present. This difference may contribute strongly to an explanation of the significant K promotion effect observed in the results presented here. Thus, it is postulated that the in the K/Pd/C reaction system discussed here that mobile formate ions in a condensed phase of HCOOH in the pores of the support material are the active species that participate in the catalytic reaction.

It is shown above that the catalytic activity of the catalyst bed comprising of a Pd/C catalyst separated by quartz wool from a K/C sample was close to the activity of the pure Pd/C catalyst. However, if the Pd/C catalyst was physically mixed with K/C a considerably improved activity close to that observed for the Pd/C catalyst impregnated
with K ions was reached. In these catalysts, potassium ions on the Pd/C catalyst particles were distinguishable by EDS, this indicating their high mobility in the reaction. This high mobility can be also provided by the formation of a condensed liquid in the pores of the catalyst that dissolves the potassium salt. For the unsupported Pd powder, the promotional effect was much lower than that with K-doped Pd/C samples; the lower level of K doping and the lower surface area may result in decreased formation of condensed formic acid. These results seem to confirm that a liquid formed in the pores of the catalyst play an important role in the formic acid decomposition.

In the proposed mechanism, both Pd and water are required for the rate-limited reaction step (Eq. 3). Normally, the decomposition of unsupported bulk alkali metal formates takes place at temperatures above 573 K. The Pd nanoparticles present on the catalysts studied lower the reaction temperature and catalyse the decomposition of the formate ions to give hydrogen and CO₂. In addition, the condensed formic acid/water solution provides easy access of the formate ions to the active Pd sites. Some literature data clearly indicate that water is also necessary for low temperature formate decomposition. Thus, Jacobs et al. [4] demonstrated that water promotes the decomposition of formate species over Pt on oxidic supports. Wang et al. [22] showed that water is really necessary for formate decomposition in the liquid phase as no decomposition of a formic acid/formate mixture took place when water was substituted by tetrahydrofuran. Additionally, Wiener et al. [23] confirmed the necessity of water by kinetic isotope effect studies in the presence of Pd/C catalyst. At the temperatures used here, as low as 353 K, at least a part of water formed in the reaction (2) probably remains in the pores of the catalysts. Water is also formed in the parallel dehydration reaction of formic acid to give CO and H₂O even though the selectivity of this reaction is very low (0.02%) at 353 K (Table 2 in Chapter 3).
4 Conclusions

This chapter reports additional results on the considerable promotional effect of alkali metal ions in hydrogen formation from formic acid decomposition. Characterisation of K-doped Pd catalyst showed there is no interaction between Pd and K doped; the dispersion of K changed after reduction/reaction in a physically mixed K-Pd/C catalyst. The early stages of the decomposition of the formic acid was studied with the K-Pd/C catalyst. It was found that a significant proportion of the HCOOH was adsorbed or condensed on the K-doped Pd/C catalyst while another proportion of the HCOOH reacted with carbonate species on the surface, both of these proportions increasing with increasing K concentration. Physically mixed K-Pd/C catalysts exhibited a similar promotion as the one prepared by the impregnation method whereas the Pd/C and K/C samples separated by quartz wool did not give any improvement in formic acid decomposition, showing the importance of intimate contact between Pd and K in giving the promotional effect. Unsupported Pd powder doped by K showed less improvement in the catalytic activity with doping and this implied that the large quantity of K used for doping is another important element. Based on all the results obtained, a reaction mechanism with three main reaction steps is proposed for the K-doped Pd/C catalysts. The second reaction step of the reaction between formate ions and water catalysed by Pd in this mechanism is rate determining. The mobility of formate ions in liquid HCOOH significantly increases the probability of contact with catalytic site Pd and therefore accelerates the decomposition of the formate, this being an essential factor in improving the allover reaction rate.


References


Chapter 5

DRIFTS study of the mechanism of formic acid decomposition over palladium based catalysts

Abstract

The introduction of potassium into Pd/SiO$_2$ and Pd/Al$_2$O$_3$ catalysts promoted both the catalytic activities and the hydrogen selectivities for formic acid decomposition, giving values of the TOF at 343 K that were 7 and 8 times higher respectively than those for the undoped samples. The apparent activation energy over all the K-doped samples increased this showing that there is a difference in the reaction path between the doped and the undoped catalysts. The DRIFTS technique has been used to gain an understanding of the nature of the adsorbed species during the reaction. This study shows that a considerable fraction of the HCOOH is condensed in the pores of the catalysts and that the existence of mobile formate ions dissolved in the HCOOH condensed in the pores of a K-doped catalyst is an essential factor in the promotion of its activity.
1 Introduction

In Chapters 3 and 4, it was shown that the introduction of an alkali metal into a Pd/C catalyst promotes its catalytic performance for formic acid decomposition. It is therefore important to study the reaction mechanism over the promoted catalysts. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is a technique typically used to give information on reaction intermediates by in-situ tests. A significant amount of work based on the DRIFTS measurements has been reported for both formic acid decomposition [1-8] and the water-gas shift reaction [9-21]. All of the papers on these topics show the great potential value of the utilization of DRIFTS method. Unfortunately however, there are restrictions as to the types of samples that can be used in DRIFTS measurements. In particular, activated carbon supports of the type used for the samples reported in the previous chapters cannot be used in DRIFTS tests because of their total absorbance of IR light; this means that any reflected IR light signal after absorbance by the activated carbon is too weak to be detected.

For this reason, and because silica is often considered to have similar properties to those of activated carbon, Pd catalysts supported on silica and doped with potassium were examined in this DRIFTS study; alumina-supported samples were also examined. Before carrying out the DRIFTS experiments reported below, catalytic measurements were carried out with the Pd/Al₂O₃ and Pd/SiO₂ catalysts to ascertain whether potassium also had a promotional effect on these samples and then to obtain comparable activity and selectivity data for these samples to those reported in the previous chapters for the C-supported materials. Full characterisation of these catalysts was also carried out. DRIFTS measurements were then carried out to examine the adsorption and
desorption of formic acid and the adsorption of CO. Based on these results, a possible mechanism for the formic acid decomposition reaction is proposed.

2 Results

2.1 Characterisation and catalytic activities of Pd and K-doped Pd catalysts supported on silica and alumina

2.1.1 Characteristics

Table 1 shows the BET surface areas and particle sizes of some of the catalysts studied in this chapter; data for the Pd/C samples reported previously in Chapters 3 and 4 are included for comparison purposes. For the Pd/C catalysts, the potassium content of the most active catalyst (10:1 K-Pd/C) was dispersed over the whole catalyst surface, the BET surface area being 933 m² g⁻¹ of Pd/C. On the basis of the lower BET surface areas of the Pd/SiO₂ and Pd/Al₂O₃ samples, weight ratio values of 4:1 for the K- Pd/SiO₂ and 2:1 for K- Pd/Al₂O₃ were adopted to make sure that the potassium ions were also evenly dispersed over the whole surface of these samples. The Pd particle size found for the silica-supported catalyst was slightly larger than those found for the samples supported on alumina and activated carbon.

Table 1: Characteristics and activity data for the catalysts used in this chapter

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BET surface area, m² g⁻¹</th>
<th>Mean particle size, nm</th>
<th>TOF at 343 K, s⁻¹</th>
<th>Activation energy, kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt.% Pd/SiO₂</td>
<td>380</td>
<td>7.4 ± 2.4</td>
<td>0.0095</td>
<td>78</td>
</tr>
<tr>
<td>4:1 K-Pd/SiO₂</td>
<td>/</td>
<td>/</td>
<td>0.079</td>
<td>95</td>
</tr>
<tr>
<td>1 wt.% Pd/Al₂O₃</td>
<td>144</td>
<td>4.2 ± 1.0</td>
<td>0.010</td>
<td>49</td>
</tr>
<tr>
<td>2:1 K-Pd/Al₂O₃</td>
<td>/</td>
<td>/</td>
<td>0.075</td>
<td>84</td>
</tr>
<tr>
<td>1 wt.% Pd/C</td>
<td>933</td>
<td>3.6 ± 1.7</td>
<td>0.008</td>
<td>65</td>
</tr>
<tr>
<td>10:1 K-Pd/C</td>
<td>688</td>
<td>3.7 ± 1.3</td>
<td>0.27</td>
<td>97</td>
</tr>
</tbody>
</table>
2.1.2 Catalytic activity

Figures 1 and 2 show the results of activity tests for formic acid decomposition over the silica- and alumina-supported Pd catalysts. Both the activity and the hydrogen selectivity of the 1 wt.% Pd/SiO$_2$ sample were slightly higher than those for the 1 wt.% Pd/Al$_2$O$_3$ sample. The curve of temperature dependence of the conversion over the 1 wt.% Pd/SiO$_2$ sample is close to that over the 1 wt.% Pd/C sample shown in Chapter 3. With both samples, K has a very clear promotional effect on both the activity and the selectivity. The TOF value at 343 K over the K/Pd/SiO$_2$ sample was 8 times greater than that of the undoped sample while the ratio was 7 for the K/Pd/Al$_2$O$_3$ sample; see Table 1. The apparent activation energies for both the oxide-supported catalysts doped by potassium increased significantly compared with the undoped materials, that showing that the reaction mechanism was changed significantly over the K-doped catalysts (Table 1). A similar promotional reaction mechanism may thus apply to all the K-doped catalysts as they all have similar activation energies, those for the C and SiO$_2$ supports both being around 95 kJ mol$^{-1}$.

![Figure 1](image_url)

**Figure 1:** Temperature dependence of formic acid conversion over undoped catalysts, Pd/SiO$_2$, Pd/Al$_2$O$_3$ and doped catalysts, 4:1 K-Pd/SiO$_2$, 2:1 K-Pd/Al$_2$O$_3$
Figure 2: Temperature dependence of hydrogen selectivity in formic acid decomposition over undoped catalysts, Pd/SiO$_2$, Pd/Al$_2$O$_3$ and doped catalysts, 4:1 K-Pd/SiO$_2$, 2:1 K-Pd/Al$_2$O$_3$

2.2 DRIFTS data for undoped and K-doped Pd/SiO$_2$, Pd/Al$_2$O$_3$ catalysts

2.2.1 Adsorption of HCOOH on Pd/SiO$_2$

A sample of 12.0 mg of the Pd/SiO$_2$ catalyst was introduced into the DRIFTS in-situ cell, this being followed by reduction in 1 vol. % H$_2$/He gas at 300°C for 1 hour. The DRIFTS cell was then cooled down in He to 333 K and HCOOH was introduced. The time dependence of the spectra obtained after introducing HCOOH are shown in Figure 3. Table 2 summarizes all the peaks observed during adsorption of HCOOH over the catalysts supported on silica and alumina. A sharp negative peak at 3740 cm$^{-1}$ and a very broad positive band ranging from 3700 to 2700 cm$^{-1}$ appeared and grew slightly with time. The appearance of the negative band in this work can be explained by the consumption of the isolated surface OH groups on silica that are attached by hydrogen bonding to the physically adsorbed HCOOH after the introduction of the HCOOH. The broad band centered at 3300 cm$^{-1}$ is characteristic of the O-H vibration in physisorbed
or condensed HCOOH. The peak with high intensity at 1739 cm\(^{-1}\) is probably mainly due to the C=O stretching mode of HCOOH adsorbed on SiO\(_2\). In the C-H stretching range, the weaker peak at 2943 cm\(^{-1}\) that can be ascribed to the \(\nu_{\text{C-H}}\) vibration of physisorbed HCOOH molecules grew slightly. A weak and broad band at 1575 cm\(^{-1}\), probably due to the asymmetric stretching vibration of the formate anion, appeared and grew slowly with time, this confirming the formation of a very small amount of formate.

**Table 2:** Summary of the vibration frequencies (in cm\(^{-1}\)) observed following adsorption of HCOOH together with the assignment of these frequencies

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Pd/SiO(_2), 4:1 K- Pd/SiO(_2),</th>
<th>Pd/Al(_2)O(_3), 2:1 K- Pd/Al(_2)O(_3),</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu(\text{C=O})) formic acid</td>
<td>1740, 1734</td>
<td>1742, 1729</td>
</tr>
<tr>
<td>(\nu(\text{CH})) formic acid</td>
<td>2943, 2938</td>
<td>2935</td>
</tr>
<tr>
<td>(\nu_{\text{as}}(\text{OCO})) formate</td>
<td>1575, 1611</td>
<td>1583, 1606</td>
</tr>
<tr>
<td>(\nu_{\text{s}}(\text{OCO})) formate</td>
<td>Not found</td>
<td>Vague</td>
</tr>
<tr>
<td>(\nu(\text{CH})) formate</td>
<td>Not found</td>
<td>2822, 2809</td>
</tr>
<tr>
<td>(2\delta(\text{CH})) formate</td>
<td>Not found</td>
<td>2716, 2700</td>
</tr>
</tbody>
</table>

Cabilla et al.[4] have reported a similar negative band to that shown in Figure 3 in their study of formic acid adsorption on a Pd/SiO\(_2\) catalyst but gave a different explanation: that it was formed by the reaction between HCOOH and isolated OH groups of the silica, producing formate species and water, the product water explaining the existence of the broad band. However, the strong asymmetric or symmetric vibrations of OCO in the range 1700-1500 cm\(^{-1}\) corresponding to the formate species was not reported by Cabilla et al. to occur in their spectra[4]. It has reported by Millar et al.[2] and by Monti et al.[22] that hydrogen-bonded monomolecular formic acid is generated after the introduction of formic acid to silica-supported Cu catalysts and this being consistent
with the explanation here. Zhang et al.[23] also reported the broad band centered at 3445 cm\(^{-1}\) when they introduced CH\(_3\)OH to a Cu/SiO\(_2\) catalyst and this being ascribed to O-H vibration in CH\(_3\)OH hydrogen bonded to Si-OH groups. They explained the sharp negative peak at 3747 cm\(^{-1}\) by the decrease of isolated Si-OH groups on the silica surface as a result of hydrogen bonding between the physisorbed CH\(_3\)OH and the Si-OH groups.

Figure 3: DRIFT spectra obtained after introduction of HCOOH within 20 min on Pd/SiO\(_2\) at 333 K

2.2.2 Desorption of HCOOH from Pd/SiO\(_2\)

Figures 4a and 4b show that a high proportion of the physisorbed HCOOH responsible for the bands at 1740 cm\(^{-1}\) and 2943 cm\(^{-1}\) and the broad peak centered at 3300 cm\(^{-1}\) were desorbed after switching off the HCOOH flow and replacing it by pure He gas at 333 K. (Figure 4b shows the results of Figure 4a on an expanded scale.) This result confirms that weak physical adsorption of HCOOH occurs on the Pd/SiO\(_2\) catalysts. As shown in
Figure 4, further desorption of physisorbed HCOOH took place as the temperature was increased; however, the peak at 1734 cm$^{-1}$ ascribed to the C=O vibration still existed even at a temperature of 453 K. Both the negative peak at 3740 cm$^{-1}$ and the broad band centered at 3300 cm$^{-1}$ disappeared with an increase in the temperature, this indicating that the desorption of HCOOH freed up once more the isolated hydroxyl groups on the silica support. It is notable that the weak but broad band at around 1600 cm$^{-1}$ could be explained by the asymmetric vibration, $\nu_{as}(OCO)$, of bridging formate species, and this showed that formate species were formed on the catalyst surface (probably on the SiO$_2$) under these conditions; the intensity of this peak did not change with increasing temperature, this showing that the adsorption bond must be quite strong.

**Figure 4a:** DRIFT spectra of adsorbed HCOOH on Pd/SiO$_2$ at 333 K and after subsequent degassing at different temperature: 333 K, 393 K, and 453 K
2.2.3 Adsorption of HCOOH over 4K-Pd/SiO$_2$

The Figure 5 shows spectra for the adsorption of HCOOH over a K-doped Pd/SiO$_2$ catalyst. As with the spectra for Pd/SiO$_2$ (see Figure 3), introduction of HCOOH to the 4:1 K-Pd/SiO$_2$ catalysts gave a sharp negative peak, related to the consumption of isolated hydroxyl groups, and a broad band due to the OH vibration of physisorbed HCOOH appeared, both bands increasing slightly with time. It is significant, however, that the intensity of the peaks ascribed to physisorbed HCOOH is much lower than that observed over undoped Pd/SiO$_2$. This is probably due to the dissociation of a significant amount of the physisorbed HCOOH molecules to give formate species as shown in the spectra. In the CH stretching range, the band at 2935 cm$^{-1}$ attributed to the CH bond in physisorbed HCOOH. The appearance of peaks at 1583 cm$^{-1}$ characteristic of asymmetric vibration of formate species confirmed the formation of formate.
results shown in Figure 5 therefore show that quite a considerable proportion of the adsorbed HCOOH dissociates into formate anions over the K-Pd/SiO$_2$ sample at 333 K.

![Figure 5: DRIFT spectra obtained after introduction of HCOOH over a period of 30 min on the 4:1 K-Pd/SiO$_2$ sample at 333 K](image)

### 2.2.4 Desorption of HCOOH from 4K-Pd/SiO$_2$

Figures 6a and 6b show spectra taken after switching from a flow containing HCOOH to He gas at 333 K and increasing the temperature to 493 K in the He gas. The C=O vibration peak at 1742 cm$^{-1}$ due to physisorbed HCOOH disappeared totally at 393 K over the K-Pd/SiO$_2$ sample in He gas and this is quite different from the result over the undoped Pd/SiO$_2$ catalyst with which a small peak still existed after heating to 453 K (Figure 4). Both the negative peak at 3740 cm$^{-1}$ and the broad band centered at 3300 cm$^{-1}$ also disappeared with increasing temperature. However, the band at 1586 - 1606 cm$^{-1}$ corresponding to a strong asymmetric vibration of a formate species was seen after introducing HCOOH to the K-Pd/SiO$_2$ catalyst and it continued to grow even after
switching from the HCOOH flow to that of pure He even while heating to 393 K. The formate species band at 1606 cm\(^{-1}\) still existed in the spectrum at 493 K.

Figure 6a: DRIFT spectra of HCOOH adsorbed on 4:1 K-Pd/SiO\(_2\) at 333 K and after subsequent degassing at different temperatures: 333 K, 393 K, 453 K, and 493 K

The expanded spectrum of Figure 6b shows that three peaks at 2937 cm\(^{-1}\), 2822 cm\(^{-1}\) and 2726 cm\(^{-1}\), corresponding to CH stretching, had appeared at 333 K during the adsorption process and that they remained during the entire desorption procedure. The band at 2937 cm\(^{-1}\) here is probably a combined peak due mainly to physisorbed HCOOH and probably some CH stretching vibration from formate species as well, the peak attenuating after switching off HCOOH to He. In agreement with the data from the lower wavenumber range, the peaks at 2809 cm\(^{-1}\) and 2700 cm\(^{-1}\) ascribed to the CH stretching of formate species became stronger after switching off the HCOOH flow and increasing the temperature to 393 K. This is consistent with the suggestion that after switching off the HCOOH and increasing the temperature to 393 K, the remained
physically adsorbed HCOOH dissociates to give H and formate species, this resulting in
the higher intensity peaks corresponding to the formate species in both the OCO and
CH stretching ranges. The C=O stretching peak of physisorbed HCOOH totally
disappeared at 393 K showing that all the adsorbed HCOOH either decomposed or
dissociated to form formate species.

**Figure 6b:** Expanded-scale spectra of Figure 6a

### 2.2.5 HCOOH decomposition at different temperatures over the 4K-Pd/SiO₂ catalyst

The Figure 7 shows DRIFTS results obtained with a 4K-Pd/SiO₂ catalyst in the
HCOOH flow at different temperatures. The peaks at 2934 cm⁻¹ and 1742 cm⁻¹ both of
which represent physisorbed HCOOH decreased with the increasing temperature
showing that more HCOOH dissociated to give formate species or decomposed at
higher temperature. However, the band at 1742 cm\(^{-1}\) representing physically adsorbed HCOOH still clearly existed at 393 K.

![Figure 7: DRIFT spectra obtained after introduction of HCOOH on 4:1 K-Pd/SiO\(_2\) at different temperature: 333 K, 353 K, 373 K, and 393 K](image)

2.2.6 CO adsorption

It is well established that a small amount of CO can poison the Pd-containing catalysts. In the present work, the introduction of potassium into the Pd/C and Pd/SiO\(_2\) materials promoted both the reactivity and hydrogen selectivity during formic acid decomposition. A comparison of CO chemisorption results showed that the amount of CO adsorbed on the undoped Pd/C catalyst was 1.5 times that adsorbed on the doped Pd/C catalyst (Chapter 3). DRIFTS experiments on the adsorption of CO were therefore carried out with the Pd/SiO\(_2\) materials to examine this difference further. Figure 8 shows the IR spectra of both the doped and undoped catalysts after the introduction of CO gas at 333
Bands were found at 1930 cm\(^{-1}\) with the Pd/SiO\(_2\) sample and at 1850 cm\(^{-1}\) with the K-Pd/SiO\(_2\) sample; both of these bands are very weak because of the low concentration of the Pd surface sites in the samples studied. For the Pd/SiO\(_2\) catalyst, the band centered at 1930 cm\(^{-1}\) with a broad shoulder to lower wavenumber seems to indicate that there is more than one form of CO adsorption on this sample. This band is typical of that for bridge-bonded CO on Pd (111)[24-27]. For the K-Pd/SiO\(_2\) catalyst, the peak was red shifted to 1850 cm\(^{-1}\), this being characteristic of a CO adsorption mode on three-fold hollow surface Pd sites[27, 28]. During the adsorption on Pd metal, the bond strength of CO decreased and this contributing to shift of bands to lower wave number compared with gas CO. No peak was found at 2050 cm\(^{-1}\); if such a peak was observed, it would be due to linearly adsorbed CO on (111)/(111) and (111)/(100) edge sites. It can therefore be concluded that there is a low concentration of such sites in the both these catalysts. All the peaks due to CO adsorption were hardly observed during HCOOH decomposition procedure, it showing the little amount of the product of CO.

**Figure 8**: Comparison of spectra after the introduction of CO gas into the catalysts with potassium and without potassium.
2.2.7 Adsorption of HCOOH on the Pd/Al$_2$O$_3$ and 2:1 K-Pd/Al$_2$O$_3$ samples

Figures 9 and 10 show the DRIFTS results obtained for adsorption of HCOOH on 2:1 K-Pd/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ using the same procedure as for the silica-supported catalysts reported in the previous sections. The spectra for both the K-doped and undoped catalysts showed similar peaks; this lack of any apparent difference could be due to the small concentration of K in the doped Pd/Al$_2$O$_3$ sample. As with the work on the silica-supported catalysts reported above, physisorbed HCOOH appeared over both the catalysts, this being responsible for the CH stretching peaks at 2936 cm$^{-1}$, 2924 cm$^{-1}$ and the C=O stretching vibration peaks at 1735 cm$^{-1}$ and 1740 cm$^{-1}$; the negative band at 3740 cm$^{-1}$ also showed up after introducing HCOOH into both the alumina supported catalysts, this indicating the consumption of the hydroxyl groups of the alumina supports. However, the broad band observed for the silica-supported material and ascribed to hydrogen bonding of physically adsorbed HCOOH if present in the case of the alumina support was too weak to be observed. Two additional strong peaks at around 1618 cm$^{-1}$ and 1400 cm$^{-1}$, typical of formate species, were visible in the spectra of both the alumina-supported catalysts. This implies that quite a large proportion of the physically adsorbed HCOOH was dissociated into formate species over these two catalysts. It is notable that these bands at around 1618 cm$^{-1}$ and 1400 cm$^{-1}$ have shoulders at lower wave numbers and this could be explained by the existence of a number of different formate species locations on the catalyst surfaces.
Figure 9: DRIFT spectra obtained at intervals after introduction of HCOOH to Pd/Al₂O₃ at 333 K

Figure 10: DRIFT spectra obtained after introduction of HCOOH within 30 min on 2:1 K-Pd/Al₂O₃ at 333 K
2.2.8 Desorption of HCOOH from Pd/Al₂O₃ and 2:1 K-Pd/Al₂O₃

Figures 11 and 12 show the DRIFT spectra obtained under the adsorption of HCOOH at 333 K and following desorption of HCOOH from both the undoped and K-doped Pd/Al₂O₃ catalysts. The peaks in CH stretching range at 2892 cm⁻¹, 2740 cm⁻¹, 3017 cm⁻¹, 2915 cm⁻¹, etc. ascribed to different formate species consistent with OCO vibration range. Compared with the results obtained for the silica-supported catalysts, the spectra for the alumina were more complicated. Peaks due to more than one type of formate species appeared and grew during this procedure. In the OCO asymmetric and symmetric ranges, the bands split into several peaks and broadened in shape. As with the results for the silica-supported catalysts, physically adsorbed HCOOH appears to be responsible for the peaks at 1733 cm⁻¹ and 2936 cm⁻¹; these species were largely desorbed after switching from a flow of HCOOH to pure He.

![DRIFT spectra](image)

**Figure 11:** DRIFT spectra of HCOOH adsorbed on Pd/Al₂O₃ at 333 K followed by degassing at different temperatures: 333 K, 393 K, 453 K, and 493 K
Figure 12: DRIFT spectra of HCOOH adsorbed on 2:1 K-Pd/Al₂O₃ at 333 K followed by degassing at different temperature: 333 K, 393 K, 453 K, and 493 K

3 Discussion

3.1 The existence of liquid HCOOH during adsorption over all catalysts used in the thesis

The results on both unsteady state study (Chapter 4) and the DRIFTS results show that a significant proportion of HCOOH introduced are physically adsorbed on all the catalysts used in this thesis. From the unsteady state study, it was concluded that a considerable fraction of the HCOOH introduced became adsorbed or condensed in a molecular state on the K-doped Pd/C catalysts. The DRIFT spectra of HCOOH adsorption showed strong bands typical of the C=O stretching of formate species together with broad bands due to hydrogen bonding of physically adsorbed or condensed HCOOH. The physisorbed HCOOH mode is shown in Scheme 1 which shows the O of the C=O group hydrogen bonded with an H (of the hydroxyl group of the silica support); there is also a small amount of HCOOH adsorbed with the O of the
C=O group directly bonded to Pd sites as shown in Scheme 1. The properties of physisorbed HCOOH tended to become the same as liquid HCOOH when the amount of adsorbed HCOOH increased. Scheme 2 depicts the formation of liquid HCOOH in the catalytic reaction system. After multiple layers of physical adsorption of HCOOH, the condensed HCOOH in the catalysts is not very different from liquid HCOOH.

![Scheme 1: Physisorbed HCOOH on SiO₂ and Pd](image1)

![Scheme 2: Schematic depiction of the formation of monolayer physisorbed and condensed/liquid HCOOH after introduction of HCOOH gas into the catalysts](image2)

### 3.2 The formation of formate intermediates on the K-doped catalysts

When HCOOH gas was introduced into the K-doped Pd catalyst, a large concentration of formate species was formed at the same time. This was confirmed by both the DRIFTS results and the earlier unsteady-state study. From DRIFT spectra, it was found that (i) strong peaks ascribed to formate species appeared; (ii) broad peaks in the higher wave number range of 3700-2700 cm⁻¹ due to hydrogen bonding in molecular HCOOH.
increased more markedly compared with the undoped Pd/SiO\textsubscript{2} catalyst. There are two feasible explanations for these DRIFTS results. One possibility is that the number of hydroxyl groups is decreased by the introduction of potassium; the potassium thus blocks some fraction of the silica surface sites [17-19] or ions exchange with the OH group giving OK groups. The other possible explanation is that introduction of potassium into the Pd catalysts increases the uptake of formic acid and induces the formation of the formate species[29]. A considerable quantity of formate species was generated in this procedure. In the unsteady state study of Chapter 4, it was speculated that the generation of formate species occurred at the beginning of the reaction and the DRIFTS results confirm this assumption.

It is notable that the peaks attributed to formate species became even stronger after switching from HCOOH to He and that the formate species peaks were stable at temperatures as high as 493 K, this showing that the dry formate species hardly decompose. It can be suggested that two different states of the formate species exist: mobile formate anions existing in liquid HCOOH before switching off the HCOOH gas; and bulk formate species crystallized after most of the HCOOH is desorbed from the catalyst surface (see Scheme 3).

**Scheme 3:** Schematic formation of bulk potassium formate after switching off HCOOH gas to He gas
Three typical adsorption modes of formate species are shown in Scheme 4. It has been shown that all of these three types of adsorbed formate species adsorbed on noble metals or metal oxides contribute CH stretching peaks in a range of 2750-3000 cm\(^{-1}\) [30]. Vibrational couplings, generally consisting of \(\nu_{as}(OCO) + \delta(CH)\), \(\nu_s(OCO) + \delta(CH)\) and \(2\delta(CH)\), sometimes also take place and this results in more peaks around the main CH stretching band. However, none of the peaks described above would be found at frequencies lower than 2700 cm\(^{-1}\). A similar peak to the one found at 2700 cm\(^{-1}\) in the spectra has been reported only in catalyst samples containing an alkali metal. Davis [16-18] explained such a peak as being due to the coupling of two CH bending vibrations and found that the peak intensity increased with an increasing alkali metal concentration. The peak at 2700 cm\(^{-1}\) appeared with the K-Pd/SiO\(_2\) catalyst in this work but it was not found over the catalyst without potassium. Solid/bulk potassium formate shows a peak at the same position, around 2700 cm\(^{-1}\), and this is consistent with the spectra reported here. It is therefore possible to conclude that surface crystalline potassium formate was formed after switching from the HCOOH-containing gas flow to a pure He flow.

**Scheme 4:** Three common adsorption modes of formate species over noble metals and several metal oxides; reproduced from references [30, 31]
3.3 The acceleration of the catalytic decomposition of formic acid in the presence of mobile formate ions

The importance of the liquid phase for the catalytic promotion was emphasized in Chapter 4. The DRIFTS results confirmed this speculation. As shown in the DRIFTS results over the 4 K-Pd/SiO$_2$ catalyst, formate ions in liquid HCOOH are more active than bulk formate species without liquid HCOOH. After switching from the HCOOH flow to He, bulk formate species crystallized from the decreasing volume of liquid HCOOH in the pores and were stable at the high temperature of 493 K. The liquid formic acid provides easy access of the formate ions to all the surface Pd sites. In addition, the DRIFTS results on HCOOH decomposition over the K-Pd/SiO$_2$ at different temperatures showed that the peak due to formate species was weaker compared with the ones found in the HCOOH desorption spectra at the same temperature, this again confirming that the mobile formate ions in the liquid HCOOH phase are an essential factor for improving reaction activity.

4 Conclusion

It can be concluded that the addition of potassium to a Pd/C catalyst promoted the catalytic activity and the hydrogen selectivity in formic acid decomposition remarkably, the reaction rate being increased by 1-2 orders of magnitude. Based on the similar activity results showing significant promotion of the K-doped Pd/SiO$_2$ and Pd/Al$_2$O$_3$ materials, DRIFT spectra of HCOOH adsorption and desorption on and from Pd catalysts supported on silica and alumina were studied to gain an understanding of the intermediate species participating in the reaction. The DRIFTS results show that the presence of potassium induces the formation of formate species and also changes the adsorption state of CO on the Pd surface site. The DRIFTS results confirmed the
mechanism proposed in Chapter 3: that the liquid phase of HCOOH and mobile formate ions are the two essential factors for the promotion of the catalysts by providing formate ions to the Pd sites in liquid HCOOH.
References


Chapter 6*

Pt Nanoclusters Stabilized by N-doped Carbon Nanofibers for Hydrogen Production from Formic Acid

Abstract

The activities of Pt catalysts on carbon nanofibers with different nitrogen contents were compared for hydrogen production by formic acid decomposition. The catalysts contained a fraction of Pt clusters with a mean size of 1.0–2.3 nm and possibly a considerable fraction of Pt clusters with a diameter of less than 0.75 nm that were invisible by transmission electron microscopy. The activities of N-doped catalysts with low Pt contents (≤1 wt.%) were 10 times higher than the activities of undoped catalysts. The N-doped catalysts demonstrated an improved selectivity to hydrogen and an increased resistance to CO inhibition. However, they were inactive for ethylene hydrogenation. These results are explained by the presence of electron-deficient, two-dimensional sub-nm sized Pt clusters stabilized by pyridinic nitrogen on vacancy sites. In accordance, the Pt-4f\textsubscript{7/2} binding energies measured by X-ray photoelectron spectroscopy were 0.6 eV higher for the N-doped samples than for the undoped ones.

* Chapter 6 has been published in Journal of Catalysis.
1 Introduction

It has been shown recently that formic acid can be produced from biomass [1]. Hydrogen production by the catalytic decomposition of formic acid has generated much interest due to the possible application of formic acid as a source of molecular hydrogen [2-8] or as a hydrogenating agent [9, 10]. The decomposition reaction has been used for over a century as a model reaction to distinguish catalysts favoring dehydrogenation (giving H₂ and CO₂) from those favoring dehydration (giving H₂O and CO). In current studies of formic acid decomposition, the main target is highly selective hydrogen production under mild reaction conditions.

Recently, Ojeda and Iglesia [6] concluded from their studies with Au/Al₂O₃ catalysts that Au species invisible by transmission electron microscopy (TEM) could be important for vapor phase formic acid decomposition. Bi et al. [5] confirmed that samples with Au species of about 0.8 nm size supported on zirconia are several times more active than equivalent samples with Au particles of about 1.8 nm size in the liquid phase decomposition of formic acid in the presence of water, triethylamine or sodium formate. Finally, Yi et al. [11] in a very recent paper demonstrated that atomically dispersed Au species on ceria are extremely active, resistant to CO and selective in vapor phase formic acid decomposition.

Stabilization of isolated metal atoms and sub-nm clusters in order to prevent sintering is a problem. Carbon nanotubes and carbon nanofibers are considered to be potential materials for use as catalyst supports owing to their unique structural and textural characteristics and to the possibility of controlling their properties during synthesis[12-15]. Doping of the carbon-based supports with nitrogen is a possible way to stabilize supported nanosized metals [16-23].
Platinum is one of the best metals for electrocatalytic reactions such as methanol or hydrogen oxidation as well as oxygen reduction. Nitrogen doping gives a considerable enhancement in the electrocatalytic activity of Pt [20, 21, 24]. These electrocatalysts normally contain large amount of Pt (5-60 wt.%) and typical mean Pt particle sizes are 2-6 nm. However, the use of nitrogen-doped carbons as supports for heterogeneous catalysts has had little attention until now, although this topic is expected to develop [16]. Recently, it is showed that N-doping of carbon nanofibers leads to some increase in the catalytic activity of 10 wt.% Pt samples in CO oxidation [13] and to an increased activity and stability of Ru catalysts in phenol wet air oxidation [25]. Kondo et al. [26] reported an increased durability of the Pt clusters supported on N-doped graphite in H2-D2 exchange reaction as compared to those on undoped graphite.

In the present work, small concentrations of Pt (0.3 and 1 wt.%) were deposited on both N-doped and undoped carbon nanofibers to obtain Pt with very small mean particle sizes ≤1.8 nm. The performance of these catalysts was compared with the performance of catalysts with 10 wt.% Pt on the same supports and with Pt powder. Here, it has been shown for the first time that the catalysts doped by nitrogen gave significantly improved rates of hydrogen production from formic acid, higher selectivity to hydrogen and enhanced resistance to CO compared with the undoped catalysts, whereas they gave strongly decreased rates for ethylene hydrogenation. These observations are explained by suggesting that a considerable fraction of the Pt species is present in the form of electron-deficient, two-dimensional sub-nm Pt clusters invisible by regular TEM (<15 atoms), these interacting strongly with the N-doped support and that these Pt species were active in formic acid decomposition while being inactive in ethylene hydrogenation. The particle sizes and electronic properties of the Pt were characterized by TEM and X-ray photoelectron spectroscopy (XPS), respectively. The results of
literature density functional theory (DFT) calculations were used to help explain the results.

2 Results

2.1 Electron microscopy study

To determine the mean particle size in the synthesized catalysts they were characterized by TEM (Figures 1 and 2, Table 1). The mean particle sizes for the 0.3 and 1 wt.% Pt catalysts were generally in the range 1.0-1.8 nm and were lower than those for the 10 wt.% Pt samples (1.6-2.3 nm) and some Pt supported catalysts on N-doped carbons reported earlier in the literature [20]. The catalysts with 1 wt.% Pt without nitrogen (1Pt/0N-CNFs) and with 7.5 wt.% N (1Pt/7.5N-CNFs) possessed quite similar mean particle sizes (1.2-1.3 nm) and equal standard size deviations. An increase in Pt content in the catalysts with 7.5 wt.% N from 1 wt.% (1Pt/7.5N-CNFs) to 10 wt.% (10Pt/7.5N-CNFs) led to an increase in the mean particle size from 1.2 to 1.6 nm (Figure 2, Table 1). The mean particle size in the catalysts with 10 wt.% Pt decreased with nitrogen doping from 2.3 to 1.6 nm.
Figure 1: TEM images of the (a) 1Pt/0N-CNFs, (b) 1Pt/3.4N-CNFs, (c) 1Pt/7.5N-CNFs and (d) 0.3Pt/7.5N-CNFs catalysts before the formic acid decomposition reaction.

Figure 2: TEM image and particle size distribution for the 10Pt/7.5N-CNFs catalyst.
Table 1: Characteristics of the studied Pt catalysts and hydrogen selectivity and activation energy for formic acid decomposition

<table>
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<tr>
<th>Catalyst</th>
<th>Pt content, wt.%</th>
<th>Mean particle size (TEM), nm</th>
<th>Mean particle size (HAADF/STEM), nm</th>
<th>Hydrogen selectivity at 50% conversion, %</th>
<th>Activation energy, kJ mol⁻¹</th>
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</thead>
<tbody>
<tr>
<td>0.3Pt/7.5N-CNFs</td>
<td>0.3</td>
<td>1.0±0.2</td>
<td>1.0±0.2</td>
<td>99.6</td>
<td>53±6</td>
</tr>
<tr>
<td>1Pt/0N-CNFs</td>
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<td>1.3±0.2</td>
<td>1.2±0.4⁷</td>
<td>96.2</td>
<td>51±8</td>
</tr>
<tr>
<td>1Pt/3.4N-CNFs</td>
<td>1</td>
<td>1.8±1.1</td>
<td>-</td>
<td>98.1</td>
<td>46±5</td>
</tr>
<tr>
<td>1Pt/7.5N-CNFs</td>
<td>1</td>
<td>1.2±0.3</td>
<td>1.0±0.2⁷</td>
<td>99.5</td>
<td>43±2</td>
</tr>
<tr>
<td>10Pt/7.5N-CNFs</td>
<td>10</td>
<td>1.6±0.5</td>
<td>-</td>
<td>96.6</td>
<td>48.7±0.4</td>
</tr>
<tr>
<td>10Pt/3.4N-CNFs</td>
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<td>2.1±0.9</td>
<td>-</td>
<td>95.2</td>
<td>56±3</td>
</tr>
<tr>
<td>10Pt/0N-CNFs</td>
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<td>2.3±1.4</td>
<td>-</td>
<td>95.6</td>
<td>63±3</td>
</tr>
<tr>
<td>Pt powder</td>
<td>100</td>
<td>9.3⁸</td>
<td>-</td>
<td>99.2</td>
<td>93±4</td>
</tr>
</tbody>
</table>

⁷ determined from the BET surface area value
⁸ after the formic acid decomposition reaction

As the mean particle size for the 0.3 and 1 wt.% Pt catalysts was close to the sensitivity of the used TEM an EDS/TEM study of the 1Pt/7.5N-CNFs and 1Pt/0N-CNFs samples was carried out and some results are shown in Figure 3. This study demonstrated the presence of several regions in the samples, where Pt particles were not clearly seen by TEM. However, Pt was seen in these regions by EDS. This generally indicates that a fraction of TEM-invisible Pt species exists in the catalysts. The invisible Pt could be present as sub-nm sized clusters or even in an atomically dispersed state. To confirm this, a study with more sensitive HAADF/STEM method was performed (Figure 4, Table 1). Two samples with 1 wt.% Pt after the reaction and one with 0.3 wt.% Pt...
before the reaction were taken for this research. The mean particle sizes determined by HAADF/STEM were quite similar to those obtained by TEM (Table 1), however, the shapes of particle size distributions were very different. The measurements by HAADF/STEM demonstrated much stronger left hand part in the distributions than in those determined by TEM. This has to be explained by higher sensitivity of this method to smaller particles (0.75-1 nm). Particles smaller than 0.75 nm can hardly be seen by this method either. No difference in the samples before and after the reaction was found.

**Figure 3:** EDS/TEM measurement of Pt concentration in the 1Pt/0N-CNFs (left) and 1Pt/7.5N-CNFs (right) catalysts

The shape of the distributions characterized by the most intensive left hand bar may indicate that a considerable fraction of clusters with a size of <0.75 nm (<15 atoms) is present in the studied samples. This is in agreement with the EDS/TEM studies (Figure 3), indicating the presence of TEM invisible clusters or atoms. This means that the particle size distributions for the N-doped catalysts obtained by regular TEM (figures 1 and 2) and HAADF/STEM (Figure 4) do not fully reflect the real picture since a major part of Pt can be invisible in both doped and undoped samples. The microscopic methods used do not allow one to discriminate the difference in the mean Pt particle sizes for the 1 wt.% Pt samples with and without 7.5 wt.% nitrogen. However, it is
important that the obtained mean particle sizes for these samples correspond to about 100% dispersion of Pt, showing that all the Pt could be available for the catalytic reaction.

Figure 4: HAADF/STEM images of the 1 wt.% Pt catalysts on the N-CNFs supports after the formic acid decomposition reaction and of the 0.3 wt.% Pt catalyst on the 7.5N-CNFs support before the reaction.
2.2 Formic acid decomposition and ethylene hydrogenation

Figure 5a shows the temperature dependence of formic acid conversion for three 1 wt.% Pt catalysts with different N contents; the catalytic activities were significantly improved by increased levels of nitrogen doping. The temperatures at which 50% conversion was achieved were 445, 475 and 518 K for 1Pt/7.5N-CNFs, 1Pt/3.4N-CNFs and 1Pt/0N-CNFs, respectively. The results of Figure 5a show that the same conversion was obtained at a temperature 73 K lower with the N-doped (7.5 wt.% N) material than with the undoped one. The hydrogen selectivities measured at 50% conversion for these samples are shown in Table 1. The selectivity hardly varied with change of temperature and conversion but it increased from 96.2% to 99.6% with an increase in the level of N-doping of the samples. A selectivity of 99.6% corresponds to a CO content of 40 ppm, a value that approaches the requirements for the application of the reaction in fuel cells.
Figure 5: (a) Temperature dependence of HCOOH conversion over the 1 wt.% Pt catalysts on the N-CNFs supports with different N content and (b) turnover frequency as a function of N content at 373 K (squares – 1 wt.% Pt, star – 0.3 wt.% Pt, triangle – Pt powder)

The turnover frequency (TOF) for the same samples with low content of Pt was calculated assuming that there was 100% dispersion of Pt. The TOF for formic acid decomposition for the 1Pt/7.5N-CNFs catalyst at 373 K was about 10 times higher than that for the undoped sample (1Pt/0N-CNFs) (Figure 5b). It can therefore be concluded that nitrogen doping significantly improves the catalytic properties. The TOFs for the N-doped samples with 0.3 and 1 wt.% of Pt were very close. This may indicate a linear increase in the concentration of active sites for the reaction in this concentration range of Pt. The activity of the Pt powder per surface Pt atom was also measured. It was about 3 times lower than the activity of the Pt/0N-CNFs catalyst.

The effect of the addition of CO on the rate of hydrogen production from formic acid decomposition was studied at 423 K with the 1Pt/7.5N-CNFs and 1Pt/0N-CNFs catalysts and the results are shown in Figure 6. The reaction rates for the both catalysts
decreased upon the introduction of CO. The decrease in the TOFs corresponded to 2.6 and 7 times for the N-doped and undoped catalysts, respectively. The TOFs for the N-containing sample in the presence of CO were even 5 times higher than those for the undoped sample without added CO. Hence, when compared with the undoped catalyst, the N-doped Pt catalyst was more resistant to CO poisoning.

**Figure 6:** The effect of CO (2.5 vol.%) on turnover frequency in hydrogen production from HCOOH decomposition over the 1Pt/7.5N-CNFs and 1Pt/0N-CNFs catalysts at 423 K

All the supports without the addition of Pt were also studied in formic acid decomposition (Figure 7). The sample without nitrogen, 0N-CNFs, showed negligible
activity for the reaction at 573 K whereas the sample containing 7.5 wt.% N, 7.5N-CNFS, gave almost complete decomposition of formic acid at this temperature. However, this temperature is about 90 K higher than that for the complete decomposition over the 1Pt/7.5N-CNFS sample (Figure 5a). This leads to the conclusion that the activities of the various supports are very low compared with those of the corresponding Pt containing materials. This is also clearly seen in Figure 8 in which a comparison is made of the reactivity of the samples supported on 7.5N-CNFSs and containing 0, 0.3, 1 and 10 wt.% of Pt. The conversion of formic acid at about 430 K over the catalyst with 1 wt.% Pt was about 40 times higher than that of the corresponding support. Thus, the data shown in Figures 7 and 8 indicate that the TOFs dependence for the Pt containing samples (Figure 5b) may not be related to the direct activity of the catalyst support in the reaction. It is seen also that the increase in the Pt content from 1 to 10 wt.% leads only to a weak increase in the formic acid conversion (by 20-30%). Hence, there is no need to increase the Pt content to a level higher than 1 wt.% to provide a highly active catalyst.

**Figure 7:** Temperature dependence of HCOOH conversion over the N-CNFSs supports with different N content.
Figure 8: Temperature dependence of HCOOH conversion over the Pt/7.5N-CNFS samples with different Pt content

The TOFs for all studied samples with Pt are shown as a function of Pt content in Figure 9. For the samples with 10 wt.% Pt, the dispersion of Pt was taken into account for calculations. The value used was based on the TEM measurements of the mean particles size (Table 1), assuming a spherical shape of the Pt particles. It is seen that the strong effect of nitrogen is observed only for the low Pt contents (0.3 and 1 wt.%), but not for the 10 wt.% Pt samples; in the latter case, the TOFs were quite similar. As was mentioned above, the mean size of Pt particles was higher for the samples with 10 wt.% Pt (Table 1).
The apparent activation energies with the 1 wt.% Pt samples decreased from 51 to 43 kJ mol$^{-1}$ with nitrogen doping (Table 1). The activation energy was considerably higher for the Pt powder and reached 93 kJ mol$^{-1}$. The values for the 10 wt. % Pt catalysts (49-64 kJ mol$^{-1}$) were slightly higher than those for the 1 wt.% Pt samples, but lower than that for the Pt powder. Solymosi et al. [7] reported an activation energy of 70 kJ mol$^{-1}$ for a 2 wt.% Pt/C catalyst with Pt particles of about 5 nm size measured for formic acid decomposition under similar reaction conditions. This value was also higher than those for the catalysts used in the thesis with lower mean particle sizes (1.0-2.3 nm) supported on carbon fibers, but lower than the value for the Pt powder (Table 1). Hence, a dependence of the activation energy on the mean Pt particle size may exist.

Ethylene hydrogenation, being a structure-insensitive reaction, is widely used to characterize the catalytic properties of supported noble metals clusters [27-31]. To understand further the effect of nitrogen doping on the catalytic properties, it has also
been studied the activities in ethylene hydrogenation of two 1 wt.% Pt catalysts, with and without N, and the results are compared in Figure 10. Unlike the behavior for formic acid decomposition, the 1Pt/0N-CNFs sample without N doping performed much better than that with nitrogen, 1Pt/7.5N-CNFs. With the former sample, all the ethylene was completely converted into ethane at 318 K. However, only 24% conversion was obtained with the 1Pt/7.5N-CNFs sample at the same temperature. The TOF corresponding to this conversion was 0.14 s⁻¹, a value much lower than those for the catalysts with relatively large Pt particles (>1.5 nm) [30, 32-34].

![Figure 10](image_url)

**Figure 10:** Temperature dependence of conversion of ethylene in hydrogenation with hydrogen over the 1Pt/0N-CNFs and 1Pt/7.5N-CNFs catalysts

Hence, doping of the carbon nanofibers by nitrogen leads to a considerable improvement of the performance of Pt catalysts with low Pt content in hydrogen production from formic acid. In contrast, the performance of the N-doped catalyst in hydrogenation of ethylene was worse than that of the undoped sample.
2.3 X-ray photoelectron spectroscopy study

The samples were examined using XPS as this method gives unique information about the state of nitrogen in the support [13, 14, 20, 35] and is sensitive to the change of metal electronic properties and particle size [25, 28, 36-38].

The N-1s spectrum of the 0.3Pt/7.5N-CNFs catalyst shows lines corresponding to three different nitrogen states (Figure 11). Pyridinic nitrogen is responsible for the line of highest intensity with a binding energy of 398.7 eV. As it is showed earlier [13, 14], for the same carbon nanofibers the concentration of this pyridinic structure increased sharply with an increase in the level of doping with nitrogen. The second main line, with a binding energy of 400.6 eV, can be attributed to graphite-like or quaternary nitrogen incorporated into the structure of an extended aromatic system (Scheme 1). These species are normally the most thermodynamically stable as compared to the others, for example, pyrrolic groups which may contribute to this binding energy region also [25]. The third peak with a binding energy of 402.7 eV was very weak and can be assigned to oxygenated nitrogen species. The C-1s spectrum showed an intensive peak at 284.7 eV typical for sp²-hybridized carbon and a peak of the shake-up satellite at about 291 eV [13]. The presence of oxygen-containing functional groups is not seen in the C-1s spectrum as the surface concentration of oxygen in the studied samples was low (4-7 at.%) as compared to some other carbon containing materials [15, 39].
Scheme 1: Nitrogen states scheme corresponding to the N 1s binding energy

Figure 11: (a) N-1s and C-1s spectra of the 0.3Pt/7.5N-CNFs catalyst
The spectra of the Pt-4f lines for the samples studied are shown in Figures 12a and 13. For the 0.3 and 1 wt.% Pt catalysts, the binding energies of Pt-4f\(_{7/2}\) increased from 71.8 to 72.4-72.6 eV linearly with increase in N content (Figure 12) and the full width at half maximum values also increased from 2.3 to 2.8-3.1 eV. An increase in the Pt content in the samples from 1 to 10 wt.% over the N-doped support (7.5 wt.% N) led to a decrease of the binding energy from 72.4 to 71.8 eV (Figures 12 and 13). Generally, measurements of the 10 wt.% Pt catalysts, as with the 1 wt.% Pt samples, showed an increase of the Pt-4f\(_{7/2}\) binding energies with nitrogen content (from 71.4 to 71.8 eV), but the binding energy values obtained were lower than those for the 1 wt.% Pt samples. Thus, as compared to the values of 71.0-71.2 eV typical for bulk metallic Pt and Pt powder (71.1 eV, used in this work), the Pt-4f\(_{7/2}\) binding energies for all Pt/N-CNFS samples were higher (Figure 12b), this indicating the presence of small Pt clusters in the samples, these probably interacting with the support.

The values of binding energy for Pt-4f\(_{7/2}\) for separate supported Pt atoms at around 73.0 eV have been reported in the literature [37, 40] while smaller values of 72.5-72.8 eV, weakly dependent on the cluster size, have been reported for sub-nm clusters with 2-6 Pt atoms [37, 41]. These binding energies are in accordance with the data for the Pt samples with 0.3 or 1 wt.% Pt and 7.5 wt.% of nitrogen (Figure 12). Pt sub-nm sized clusters with fewer than 15 atoms are hardly visible using regular TEM and HAADF/STEM.
Figure 12: (a) Pt-4f spectra (color lines – fitting with Doniach-Sunjic function) and (b) binding energy of Pt-4f$_{7/2}$ as a function of N content for the Pt catalysts on the N-CNFs supports and for the Pt black powder.

Figure 13: Pt-4f spectra for the 1Pt/7.5N-CNFs and 10Pt/7.5N-CNFs catalysts (color lines – fitting with Doniach-Sunjic function)
The Pt-4f spectra obtained could be fitted nicely by an asymmetric Doniach-Sunjic type function [13, 42] (Figure 12a and 13), this indicating that Pt is present mainly as a single state. This function is often used for description of the spectra of metallic particles. The deconvolution of some Pt-4f spectra has also been performed in the literature using symmetric Gaussian and Lorentzian functions for two or three states of Pt [43]. However, it is failed to get a good fit of the Pt spectra using this approach.

The presence of some oxidized Pt species on the surface of the catalysts cannot be excluded since the samples were contacted with air before the measurements. To understand further the state of Pt in the samples, it has been performed an XPS study of the 1Pt/7.5-CNFs catalyst before and after reduction in hydrogen for 2 h at 573 K. The treatment performed was expected to reduce any oxidized Pt present in the catalyst. In these experiments, the sample was not contacted with air after the reduction. Figure 14 shows that the binding energies for Pt-4f shifted 0.5 eV to lower values from 72.6 to 72.1 eV after the reduction. This shift is not so significant to indicate that Pt was in the form of bulk oxide initially. It is more likely related to removal of chemisorbed oxygen as well as to sintering of some sub-nm sized Pt clusters during the reduction. The value of 72.1 eV was much higher than that for the bulk Pt (71.1 eV), this indicating that the Pt was still present in the form of sub-nm sized clusters after the reduction. This value was also higher than the value for the unreduced Pt catalyst (71.8 eV) with the same Pt content but without nitrogen (Figure 12). It is interesting that the spectrum of Pt after the reduction was still asymmetric and could be described with the Doniach-Sunjic function with an asymmetry parameter of 0.09, a value quite similar to that used for the description of the spectra obtained for the sample before the reduction (0.12).
Summarizing, the XPS results confirmed the presence of highly dispersed state of Pt in the samples supported on carbon nanofibers. The nitrogen doping of the support and decrease of Pt content in the samples led to a change of the Pt state to more electron-deficient state provided probably by a stronger interaction with the support.

Figure 14: Pt4f spectra of the 1Pt/7.5N-CNFS catalyst before and after reduction in H2 at 573 K (The sample was not contacted with air after the reduction)

3 Discussion

All studied Pt catalysts supported on carbon nanofibers provided a higher activity (TOFs) in hydrogen production from formic acid and lower activation energies than those for the Pt powder (Table 1, Figure 5b). It is found a considerable difference in the catalytic activities of the N-doped and undoped catalysts with low Pt content (0.3 and 1 wt.%) (Figure 9). Thus, the N-doped catalyst showed a 10 times higher TOF (Figure 5b), this being accompanied by an increased selectivity to hydrogen (Table 1) and higher resistance to CO inhibition (Figure 6). In contrast, the activity of this catalyst in
ethylene hydrogenation was considerably lower (Figure 10). These catalytic data cannot be explained by direct participation of the support in the reaction as the activity of the support was negligible as compared to the activity of the Pt catalysts (Figure 8). Maiyalagan et al. [24] mentioned three possible reasons to explain an enhanced electrocatalytic activity of Pt supported on N-doped carbon nanotubes in methanol oxidation: higher dispersion of Pt on N-doped material, appearance of new active sites on metal-support interface and strong metal support interaction. These reasons should be taken into account for explanation of the improved catalytic performance of the Pt catalysts supported on N-doped carbon nanofibers in hydrogen production from formic acid.

3.1 Pt clusters on carbon nanofibers

Siburian et al. [44, 45] and Yoo et al. [46] have reported that the formation of sub-nm sized Pt clusters takes place on the undoped graphene surface but not on other carbon materials [44]. TEM and HAADF/STEM studies of 0.3 and 1 wt.% Pt catalysts supported on carbon nanofibers demonstrated the presence of clusters with about 1 nm size stable in hydrogen at least at 573 K. The presence of a considerable fraction of clusters with the size of less than 0.75 nm is very probable as shown by EDS/TEM experiments Figure 3) and from the shapes of the particle size distributions obtained by HAADF/STEM (Figure 4). XPS data (Figure 12b) were also in accordance with such small size of Pt clusters. It is observed a significant shift, by 0.6 eV to higher values, in the Pt-4f\(\gamma/2\) binding energies for the N-doped samples (Figure 12b). Initial and final state effects should be taken into account to explain this shift. The initial state effects are determined by the electronic structure of the clusters, this being related to the metal-metal coordination number and/or interaction with the support [36, 45]. The final state
effects are determined by the size of the cluster supported on carbons and oxides and imply a linear dependence of the binding energy value on the inverse of the size of metal particles [28, 36, 38].

Examination of the 10 wt.% Pt samples indicated an improved dispersion of the Pt particles on the N-doped carbon nanofibers as compared to those on the undoped nanofibers (Table 1). This was in line with literature data [13, 20, 21]. In contrast, significant differences were not found in the Pt particle sizes in the N-doped and undoped samples with 0.3 and 1 wt.% Pt (Figure 4, Table 1). It has been shown that the formation of sub-nm sized Pt clusters may take place on the both N-doped and undoped carbon nanofibers if a low concentration of Pt is used. This does not allow us to explain the considerable differences in the Pt-4f\textsubscript{7/2} binding energy (Figure 12) or in the catalytic activity (Figures 5, 9 and 10) by invoking a particle size effect.

As the mean size of Pt in the samples with low Pt concentrations studied was quite similar, the higher binding energies of Pt in the N-doped samples indicate the presence of more electron-deficient Pt clusters as compared to the undoped samples. The electron-deficiency of these Pt clusters decreased with the increase in the Pt content and clusters size of the samples (Figures 12b and 13). This takes place as a smaller fraction of Pt atoms interacts with the support. It is reasonable to propose the existence of three-dimensional clusters in the case of weak interaction with the support. The formation of two-dimensional clusters is preferable in the presence of strong cluster-support interaction. Pt atoms in three-dimensional clusters have a higher average coordination number than those in lower dimensional clusters and processes of extra-atomic relaxation take place more effectively. This means that with the same number of atoms in a cluster, a positive shift of binding energies for a three-dimensional cluster will be
smaller as compared to the shift for two-dimensional clusters. Thus, XPS data may indicate that two-dimensional, electron-deficient sub-nm sized Pt clusters are formed on the N-doped carbon fibers with low content of Pt. In accordance, Kondo et al. [26] found by STM that N-doping of graphite stabilized monolayer (two-dimensional) sub-nm sized Pt clusters. These authors also showed that such clusters on undoped graphite transformed to three-dimensional clusters. The enhanced durability of the two-dimensional clusters on the N-doped carbon was assigned to increased interface interaction owing to electron doping.

Generally, the stability of metal clusters could be an important feature affecting the decision of using these materials as catalysts. The stability of clusters can be dependent on gas composition and on interaction with the support provided by the presence of specific surface sites. A strong interaction of Pt with the support prevents Pt diffusion and sintering. It was found that the sub-nm sized Pt species supported on N-doped carbon nanofibers were stable in hydrogen at least at 573 K. Yoo et al. [46] and Cho et al. [47] showed similar or even higher stabilities of sub-nm Pt clusters on graphene surface. Introduction of defects [19, 48] or nitrogen doping [17-19] could further increase the stability of such Pt species. The sites between the graphite layers could be also important places for location of thermally stable sub-nm clusters [12, 47]. Hence, a consideration of possible sites of the support determining the stability of Pt clusters is necessary.

As it is showed by XPS, graphitic and pyridinic N atoms exist in the N-doped catalysts (Figure 11). The graphitic nitrogen atom is attached to three carbon atoms and takes the planar structure of graphite. This nitrogen is considered as an electron donor [49, 50]. Li et al. [18] showed that the carbon system with graphitic nitrogen may interact with Pt
atoms stronger than undoped graphene. The graphitic N atoms avoid bonding to Pt directly. The activation of carbon atoms close to nitrogen atoms for interaction with sub-nm Pt clusters and stabilization of these clusters takes place due to a large electron affinity of neighboring nitrogen atoms. At the same time, Li et al. [18] showed that interaction of Pt with the carbon system containing graphitic N atoms is weaker than that with the carbon system containing pyridinic N atoms on vacancy sites.

The pyridinic nitrogen atom is attached to two carbons. Its presence is often associated with defect sites on edges of graphite layers [20, 35] or on vacancy sites [18, 50]. The pyridinic nitrogen is negatively charged [51]. A significant negative charge follows from a significant negative shift of the N-1s binding energy (1.9 eV) with respect to that of graphitic nitrogen (Figure 11). The pyridinic nitrogen on vacancy sites is an electron acceptor [49, 50]. It was supposed already that this nitrogen can be mainly involved in the sites for strong interaction with Pt [17, 18, 20, 21] decreasing electron density on Pt [52].

It has been observed by Raman spectroscopy an increase in the concentration of defects in the studied carbon nanofibers having a herringbone structure with increase in the concentration of pyridinic atoms [53]. This indicates that the formed pyridinic nitrogen in supports is mainly related to vacancy sites. During preparation of the catalysts, high accessibility of the surface support sites to Pt containing intermediates is achieved for graphene and carbon nanotubes supports. The high resolution TEM studies [14] showed that introduction of nitrogen to carbon fibers stabilized the open edge graphite planes leading also to their high accessibility. Two graphite layers with pyridinic nitrogen on vacancy sites could be considered as traps for Pt clusters located between them. A donor-acceptor interaction of Pt clusters with such sites may lead to a two-dimensional
shape of these clusters. As this interaction could be very strong, it is difficult to assume that the Pt intermediates would move too deeply between the graphite planes to make Pt inaccessible to reactants.

Hence, a considerable change of the Pt binding energy observed by XPS could be determined by the formation of electron-deficient, two-dimensional sub-nm sized Pt clusters attached via donor-acceptor bonds to pyridinic nitrogen atoms on vacancy sites.

### 3.2 Adsorption and catalytic properties of Pt clusters on carbon nanofibers

The electron-deficient state of two-dimensional sub-nm sized Pt clusters provided by strong interaction with the nitrogen-containing support determines adsorption and catalytic properties of Pt affecting the heats of adsorption of reactants/products as well as activation energies of reaction steps. In accordance, Kondo et al. [26] showed that two-dimensional Pt clusters supported on graphite were an order more active in the H$_2$-D$_2$ reaction than three-dimensional clusters.

Tolerance to CO is essential for any catalyst containing a noble metal to be used in formic acid decomposition since CO is one of by-products of the reaction and thus has the potential to poison the catalyst and reduce its activity. It is showed that although the active sub-nm Pt clusters on the N-doped carbon fibers could be poisoned by CO (Figure 6), the resistance to the poisoning by CO was significantly improved as compared to the less electron-deficient Pt clusters that are predominant in the sample without nitrogen. This could be understood by suggesting that there is a competitive interaction of CO and pyridinic nitrogen atoms of the support with a Pt cluster. The observed increased resistance to CO of the Pt-containing N-doped carbon nanofibers is
in accordance with *ab initio* calculations for Pt$_{13}$ clusters dispersed on nitrogen doped graphene performed by Kim et al. [19]. Tang et al. [54] showed by DFT calculations that CO adsorbed with smaller adsorption energy on a positively charged (electron-deficient) Pt$_4$ cluster than on a neutral or negatively charged cluster. In accordance, Oh et al. [55] showed experimentally that there was a strong reduction of CO adsorption energy for two-dimensional Pt clusters on graphite as compared to bulk Pt. This observed decrease of the CO adsorption was assigned to increased interaction of Pt with the support. The difference in CO interaction with the N-doped and undoped Pt catalysts can affect the dependence of the TOFs on N content in formic acid decomposition (Figure 5b) but can hardly be the only reason for this dependence.

Ethylene hydrogenation is a structure-insensitive reaction for various Pt catalysts containing metal particles with over 1.5 nm size [30, 32-34]. For such catalysts, a TOF of 2-12 s$^{-1}$ can be achieved at about room temperature. The value of the TOF for 1Pt/7.5N-CNFs catalyst was only 0.14 s$^{-1}$ at 318 K. Generally, the rate of ethylene hydrogenation over sub-nm clusters is decreased as compared to larger metal particles [28, 30, 31]. For example, Masson et al. [28] have indicated that a fall-off of ethylene hydrogenation activity takes place with Pt cluster sizes below 0.6 nm. Lu et al. [27] demonstrated that the hydrogenation may take place on isolated supported Ir atoms but only with a very low activity. Thus, the very low TOF value obtained for the 1Pt/7.5N-CNFS sample confirms the presence of clusters with a few Pt atoms in the catalyst.

The decrease of activity with the decrease of cluster size could be explained by the necessity for an ensemble of several surface Pt atoms for ethylene hydrogenation taking place via the noncompetitive Horiuti-Polyani mechanism involving interaction of ethylene and hydrogen from adsorbed states [34]. Thus, it is possible that the number of
Pt atoms is not sufficient to create such ensemble at the surfaces of some sub-nm clusters. The electronic properties of the clusters can also be important. Jackson et al. [29], in agreement with the hydrogenation data, reported that electron-deficient Pt clusters show considerably diminished activity in hydrogenation of ethylene, butadiene and butyne. They assigned this to decreased adsorption of hydrogen on such clusters.

It has been shown for the catalysts with low Pt content that in contrast to hydrogenation of ethylene (Figure 10) hydrogen production from formic acid is considerably increased with N-doping of the support (Figures 5 and 9). This result can be explained, at least in part, by different site requirements for the two reactions: the necessity of a larger ensemble of Pt atoms for hydrogenation than for formic acid decomposition. The increased activity could be reasonably assigned to the presence of under-coordinated surface Pt atoms.

Evidence of increased activity of atomically dispersed Au [11] or TEM invisible sub-nm sized Au clusters [5, 6] in hydrogen production from formic acid has recently been reported. Generally, some homogeneous catalysts such as Ru or Ir complexes have shown considerably higher TOFs in liquid phase decomposition of formic acid than do heterogeneous catalysts containing noble metal particles [2, 8]. These results support the idea that electron-deficient sub-nm sized Pt clusters or even atomically dispersed Pt could be more active in hydrogen production from formic acid than bulk Pt powder (Figure 5) or larger Pt clusters (Figure 9). Additionally, the dominating pyridinic nitrogen of the support (Figure 11) may facilitate the dissociation of the O-H bond in formic acid to give surface acid/base adducts such as that shown in reaction (1):

\[ \text{NH} + \text{HCOOH} \rightarrow \text{NH}^{+}\text{HCOO}^- \]  \hspace{1cm} (1)
These adducts can be further transformed on neighboring sub-nm Pt clusters to give hydrogen and carbon dioxide. Similar promotional effect of amines for the liquid phase formic acid dehydrogenation reaction has been reported [2, 5, 8]. Thus, it cannot be excluded that the support may activate the reactant formic acid, hence leading to improved catalytic activity. However, this demands further investigation.

4 Conclusions

It has been found that electron-deficient, two-dimensional sub-nm sized Pt clusters that are stable in hydrogen at least up to 573 K exist in Pt-containing catalysts supported on N-doped carbon nanofibers in addition to larger Pt clusters. These catalysts have an order of magnitude higher activity for the production of hydrogen by formic acid decomposition than has a catalyst prepared on carbon nanofibers without N-doping, even though both catalysts have similar TEM-visible mean particle sizes. In contrast, the undoped sample had a greater activity for ethylene hydrogenation than the sample based on the N-doped support, this suggesting that the electron-deficient sub-nm sized Pt clusters are inactive in the hydrogenation reaction. It has also been found that the catalysts based on the N-doped support had improved selectivity to hydrogen and improved resistance to CO poisoning. Finally, it can be concluded that N-doped carbon nanofibers are promising supports for stabilizing of sub-nm clusters of noble metals. The results obtained may open new routes for the preparation of novel active and selective catalysts for hydrogen production from formic acid as well as for other reactions.
Reference


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Chapter 7

Conclusion

A study of hydrogen production by the catalytic decomposition of formic acid was carried out over Pd-based and Pt-based catalysts and the results are reported in this thesis. For the work with Pd based catalysts, alkali metal ions, Li, Na, K and Cs, were doped into a 1 wt.% Pd/C catalyst. Both the activity and the hydrogen selectivity for formic acid decomposition were improved over the catalysts doped with the alkali metal ions. The doping effect follows the order K≥Cs>Na>Li. With the optimum sample containing 10 wt.% K in 1 wt.% Pd/C, the steady-state TOF at 353 K was found to be 1 s⁻¹, this value being 65 times higher than that for the undoped material. Increased hydrogen selectivity with doping gave a content of CO in the products less than 30 ppm, this meeting the requirement for the direct application formic acid as a fuel in a hydrogen fuel cell. The catalytic activity and the hydrogen selectivity were stable throughout a 22-hour activity test over a 10 wt.% K-doped Pd/C catalyst.

The doping of alkali metal ions into Pd/C catalysts changed the BET surface area, the value decreasing with an increasing content of doping ions. TEM/EDS results showed that the K in the doped Pd/C samples is dispersed uniformly over the entire catalyst surface and that the Pd particle sizes did not change with K doping. XPS tests illustrated that there is no interaction between the K and Pd.

It was found that a K-doped activated carbon without any noble metal was inactive in formic acid decomposition. When two samples, one of K/C and the other of Pd/C, were introduced to the reactor, these being separated by quartz wool, the measured activity was similar to that for a Pd/C catalyst without any promotion. These two tests results show that both Pd and K are involved in the reaction and intimate contact between Pd
and K is necessary to give promotion of the reaction. When K-doping of a Pd powder was carried out, an improvement of catalytic activity by less than 10 times was observed. The doping effect of K increased with increasing K content in doped Pd powder up to 0.3 wt.%. All the results for K doping of a Pd catalyst (with or without C support) showed that the K gave a significant increase of the apparent activation energies; over the Pd/C catalysts, the activation energy increased from around 65 kJ mol\(^{-1}\) to 97 kJ mol\(^{-1}\) and over Pd powder catalysts, the increase was from around 60 kJ mol\(^{-1}\) to 100 kJ mol\(^{-1}\). Experiments on the water-gas shift (WGS) reaction showed a similar promotional effect with K-doped Pd/C and Pt/C catalysts; in contrast, it was found that methanol decomposition was less influenced by doping the catalysts with K.

All the activity tests over the K-doped Pd/C samples that steady-state results were only achieved after some time of operation. A study of this unsteady state transition helped give an understanding of the reaction mechanism of the promoted catalyst. During the early stage of introducing the HCOOH into the catalysts, a significant proportion of the HCOOH was consumed by decomposition, reaction with carbonate species and physical adsorption. The amount increased with an increased concentration of doped K. Combining these observations with DRIFTS measurements, it is speculated that liquid HCOOH exists in the reaction system and that more formate species are generated over the K-doped Pd catalysts compared with the undoped samples. Bulk formate was crystallized during the desorption procedure of HCOOH of the DRIFTS measurements and this is stable at the relatively high temperature of 493 K. These results imply that the existence of formate ions in liquid HCOOH within the pores of the catalyst is an essential factor in accelerating the reaction rate.

The formates of Li, Na, K and Cs have similar solubilities order in formic acid or water as the one of catalytic activities; it may provide an explanation for the order of the
doping effect of the alkali metal ions. A reaction mechanism over the promoted K-doped Pd/C catalysts is proposed on the basis of both activity and characterization measurements, this consisting of three main reaction steps.

\[ K_2CO_3 + 2HCOOH \rightarrow 2KCOO + H_2O + CO_2, \]  
\[ KHCOO + H_2O \rightarrow H_2 + KHCO_3, \]  
\[ HCOOH + KHCO_3 \rightarrow KCOO + H_2O + CO_2. \]

The carbonate of the freshly prepared catalyst reacts with HCOOH at the very beginning of the introduction of HCOOH into K-doped catalysts and formate species are generated together with CO\(_2\) and water; this step can be carried out at temperatures lower than 333 K. The mobile formate ions in condensed/liquid HCOOH adsorbed in the catalyst pores then give H\(_2\) at the surface of Pd particles in the presence of water. The bicarbonate produced from the latter step then reacts with HCOOH to form formate ions once again and this completes the reaction cycle.

An investigation of Pt-based catalysts supported on N-doped carbon nanofibers was also carried out. It was found that electron-deficient, two-dimensional sub-nm sized Pt clusters were stable in hydrogen at least up to 573 K on these Pt-containing catalysts in addition to larger Pt clusters. A higher activity for the production of hydrogen by formic acid decomposition was found on these N-doped Pt catalysts than for a catalyst prepared on the carbon nanofibers without N-doping, even though both catalysts had similar TEM-visible mean particle sizes. In contrast, the undoped sample had a greater activity for ethylene hydrogenation than had the sample based on the N-doped support, this suggesting that the electron-deficient sub-nm sized Pt clusters are inactive in the hydrogenation reaction. It was also found that the catalysts based on the N-doped support had an improved selectivity to hydrogen and improved resistance to CO
poisoning compared with the material without nitrogen. It can be concluded that N-doped carbon nanofibers are promising supports for stabilizing of sub-nm clusters of noble metals. The results obtained may open new routes for the preparation of novel active and selective catalysts for hydrogen production from formic acid as well as for other reactions.