

# Formic acid decomposition over palladium based catalysts doped by potassium carbonate

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## **Abstract**

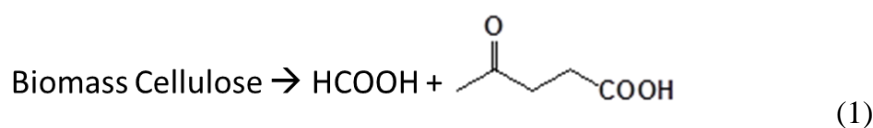
The introduction of potassium carbonate into Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/SiO<sub>2</sub> and Pd/C catalysts promoted both the catalytic activities and the hydrogen selectivities for the vapor-phase formic acid decomposition, giving values of the turnover frequency (TOF) at 343 K that were 8-33 times higher than those for the undoped samples. The apparent activation energies over all the K-doped samples increased considerably; this showing that there is a difference in the reaction path between the doped and the undoped catalysts. The Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) has been used to gain an understanding of the nature of the species formed in the Pd/SiO<sub>2</sub> catalysts during the reaction. This study showed that a considerable fraction of HCOOH was condensed in the pores of the catalysts and the introduction of potassium contributed to the formation of buffer-like solution. The existence of mobile formate ions present in the buffer solution and stabilized by K ions in a K-doped catalyst is an essential factor in the promotion of its activity.

## **Keywords**

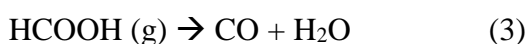
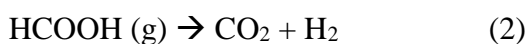
Hydrogen production; Decomposition of formic acid; K-doped Pd catalysts; buffer solution, DRIFTS

# 1. Introduction

Formic acid is a relatively low-volume chemical and it has limited uses; these include its application as a preservative and antifungal agent as well as in the production of leather and as a lime scale remover. It may be produced by chemical methods such as the hydrolysis of methyl formate but it is also produced in equimolar proportions, together with levulinic acid, by the hydrolysis of biomass-derived cellulosic raw materials [1]:



With the current increase in interest in the production of levulinic acid and other valuable chemicals from biomass, it becomes important to develop ways of using the by-product formic acid as this is otherwise a waste material. For many years, the decomposition of formic acid according to Eqs. (2) and (3):



was used as a test reaction to distinguish between catalysts with dehydrogenation (Eq.2) and dehydration (Eq.3) properties [2,3]. More recently, however, there has been considerable interest in the use of the decomposition reaction as a means of producing pure hydrogen for use, for example, in fuel cell applications; in this work, the main aims are to produce predominantly hydrogen and CO<sub>2</sub>, with minimal CO contents, at as low a temperature as possible [4-9]. In our initial work, we showed that a commercial Pd/C catalyst gave 100% conversion of formic acid vapor at a temperature of 433 K with selectivity to hydrogen and CO<sub>2</sub> of 95-99% [10]. We also showed that it was possible to

use the same catalyst to hydrogenate an olefin with formic acid stoichiometrically at the same temperature [11].

More recently, we have been probably first to demonstrate that the rate of formic acid vapor conversion over a Pd/C catalysts could be increased very significantly by the introduction of alkali metal ions into the catalyst and that the hydrogen and CO<sub>2</sub> selectivities were also increased very significantly by the alkali promotion [6,12]. We presented evidence showing that the promotional effect in K-promoted Pd/C catalysts is due to the presence in the pores of the support of a buffer solution consisting largely of potassium formate and formic acid [6]. We suggested that the rate-determining step in the decomposition reaction is the decomposition of formate anions at the surface of the Pd crystallites; as soon as a formate anion decomposes, it is replaced by the dissociation of a formic acid molecule, the concentration of the latter being replenished constantly from the gas phase. Evidence for this mechanism was obtained by careful observation of changes in the gas phase composition occurring during the early stages of the reaction prior to the establishment of steady-state behavior. Despite attempts to observe the reacting species using infrared techniques, we were unable to do this because of the lack of transparency to IR radiation of the carbon support.

The aim of the work presented in this paper was initially to examine whether or not palladium supported on an infrared-transparent material such as silica or alumina is an effective catalyst for the decomposition of formic acid and whether or not such materials can then be promoted by the addition of K<sup>+</sup> ions. Then, having shown that the Pd/SiO<sub>2</sub> catalyst gave significant rates of formic acid decomposition with good selectivity to hydrogen and that K<sup>+</sup> also gave significant promotion with this material, further experiments using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

were carried out and the results, which support the mechanism previously postulated, are also presented. The value of the use of in-situ infrared spectroscopy has previously been demonstrated for formic acid interaction with supported metals [9,13,14].

## 2. Experimental

The unpromoted catalysts used in this work were supplied by Johnson Matthey (1.0 wt.% Pd/SiO<sub>2</sub>, 1.0 wt.% Pd/Al<sub>2</sub>O<sub>3</sub>) and Sigma-Aldrich (1.0 wt.% Pd/C). The incipient wetness impregnation method was used to deposit potassium carbonate on each of these Pd-containing samples [6,12]. The measurements of catalytic activities for formic acid decomposition in the vapor phase were carried out in a fixed-bed flow reactor. The weight of the catalysts was chosen to give 0.68 mg of Pd for each set of experiments. All the samples were reduced in 1 vol.% H<sub>2</sub>/Ar at 573 K for 1 h and cooled in He to the reaction temperature prior to testing. A mixture of 2 vol.% formic acid in He at a total flow rate of 51 cm<sup>3</sup> (STP) min<sup>-1</sup> was then introduced into the reactor system 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. The details of the activity tests carried out were given in refs. [7,10].

A SpectraTech-0030 DRIFTS “in situ” cell was used for the infrared measurements, this being fitted with ZnSe windows. The cell was mounted in a Nicolet Magna 560 FT-IR spectrometer with an MCT detector; it was attached to the same gas-flow system used for the catalytic measurements and the same pretreatments, flow rates and gas compositions were used. A sample of the catalyst (Pd/SiO<sub>2</sub>, 12.7 mg or K-Pd/SiO<sub>2</sub>, 16.8 mg) to be examined was introduced into the sample holder of the cell and it was reduced in a flow of 1 vol.% H<sub>2</sub> in Ar at 573 K for 1 h. The sample was then cooled in the He flow

and single beam scanning was carried out at several temperatures to provide background spectra for the subsequent in-situ catalytic measurements at the corresponding temperatures. A 2 vol.% formic acid/He mixture was then introduced into each catalyst sample at 333 K and absorbance spectra were recorded as a function of time until stable spectra were obtained (30 min). Finally, the formic acid containing feed gas was replaced by pure He and the temperature was then increased. The corresponding absorbance spectrum at each temperature was recorded until it did not change with time.

The Brunauer-Emmet-Teller (BET) surface areas of all the samples after pretreatment in a flow of nitrogen at 473 K for 2 h were measured by nitrogen adsorption using a Micromeritics Gemini system. Transmission electron microscopy (TEM) images were obtained for the reduced catalysts with a JEOL JEM-2100F (200 kV) microscope.

## **3. Results**

### **3.1 Characterization of catalysts**

Table 1 shows the BET surface areas and particle sizes of the catalysts studied. The BET surface area of the Pd/C sample was  $933 \text{ m}^2 \text{ g}^{-1}$ , a factor of 2.5 times higher than that of the Pd/SiO<sub>2</sub> sample and 5 times higher than that of the Pd/Al<sub>2</sub>O<sub>3</sub> sample. We showed in our previous work [6,12] using a C support that a very high potassium content corresponding to a weight ratio of 10:1 of K:Pd gave the most active catalyst with even distribution of K ions through the sample. On the basis of the BET surface areas of the Pd/SiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> samples, we therefore chose to prepare samples with weight ratio values of 4:1 for the K-Pd/SiO<sub>2</sub> and 2:1 for K- Pd/Al<sub>2</sub>O<sub>3</sub> to ensure that the potassium ions were also evenly dispersed over the whole surface of these samples; no further attempts were made to optimize the K/Pd ratios. The average Pd particle size obtained from TEM

images for the silica-supported catalyst is around 7.4 nm, which is larger than those found for the samples supported on alumina (4.2 nm) and activated carbon (3.6 nm) shown in Table 1.

## 3.2 Catalytic activity data

Figure 1 (a) shows the results of activity tests for formic acid decomposition over the carbon-, silica- and alumina-supported Pd catalysts as well as the corresponding data for the K-promoted samples while Figure 1 (b) shows the values of the corresponding selectivities to hydrogen. The catalytic behavior of the Pd/SiO<sub>2</sub> sample was close to that of the Pd/C sample, the conversions for the former sample being only slightly lower than those for the latter at all temperatures; the reaction temperatures required to give 50% conversion of the formic acid over Pd/SiO<sub>2</sub> and Pd/C were both around 385 K. The Pd/Al<sub>2</sub>O<sub>3</sub> sample was significantly less active than the other two samples; the temperature for 50% conversion was approximately 30 K higher. The differences in selectivities were even more marked: the hydrogen selectivity remained above 92% at all temperatures examined over both the Pd/SiO<sub>2</sub> and Pd/C catalysts while those for the Pd/Al<sub>2</sub>O<sub>3</sub> sample fell in the range of only 79-83%.

Similar time-dependent effects during the start-up phase as those found with the K/Pd/C catalysts [6] were observed with the K/Pd samples supported on silica and alumina examined here; these effects have not been quantified. When the catalyst samples were doped with K, there was marked improvement in the steady-state behavior over each of the materials. As reported previously, the temperature necessary to give 50% conversion for the 10K-Pd/C sample is approximately 50 K lower and 100% conversion was obtained at a temperature of about 350 K. With both the silica and alumina supports,

50% conversion is now obtained at about 360 K and 100% conversion also occurs at significantly lower temperatures compared with the unpromoted materials; although the alumina-supported material is not as effective as the silica-supported one at higher temperatures, the improvement compared with the unpromoted sample is much more significant. Similar considerable improvements are found in the selectivities towards hydrogen with all three samples: all give hydrogen selectivities well above 96% for the whole range of temperature examined. The improvement in the hydrogen selectivity is particularly marked for the alumina-based sample. Generally, both the activity and hydrogen selectivity were improved by doping K ions into all the Pd catalysts with different supports.

Table 1 includes the catalytic results obtained for the three different materials without and with K as promoter, showing the values of the turnover frequency (TOF) calculated for each sample at a temperature of 343 K (calculated on the basis of the metal particle size determined by TEM) as well as the activation energies ( $E_a$ ) calculated from the Arrhenius plots. As discussed above, the TOF values show quite clearly the significant promotion by potassium species for all three supports. Particularly significant are the values of the activation energies; while for the unpromoted samples, there are significant differences between the different samples, the values for the K-promoted materials are all very similar, lying in the range 84-97 kJ mol<sup>-1</sup>. Particularly noteworthy are the values of 97 and 95 kJ mol<sup>-1</sup> obtained for the carbon- and silica-supported samples. We have previously reported a similar increase of the measured activation energies as a result of K-doping of an unsupported Pd powder [6], this set of observations indicates that promotion with K ions affects the behavior of the Pd catalysts mainly through Pd sites rather than through support sites. Not only does the change in the values of  $E_a$  indicates



that there is a change in mechanism upon doping the samples with K but that there is probably a similar promotional reaction mechanism for all the K-doped catalysts.

### 3.3 DRIFTS Measurements

In order to obtain further evidence for the mechanism proposed previously for the K-promoted Pd/C samples [6], we have carried out infrared (IR) spectroscopy measurements using a DRIFTS cell under conditions closely resembling the normal reaction conditions used in the flow reactor as described above. 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 our previous work [6,10,12] cannot be used in DRIFTS measurements because of their total absorbance of IR energy; this means that any reflected IR energy 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, the Pd/SiO<sub>2</sub> catalysts discussed above were examined in this work. Figures 2-4 show the DRIFT spectra obtained for the experiments carried out with the Pd/SiO<sub>2</sub> and K-Pd/SiO<sub>2</sub> samples. In the experiments shown in Figures 2 and 3, the formic acid was admitted at 333 K and the sample was subsequently heated in He in the absence of formic acid while in that shown in Figure 4, the sample was heated in the presence of formic acid. Each figure includes only those parts of the spectra that show significant features, these appearing in the regions 4000 to 2800 cm<sup>-1</sup> (a region containing bands associated with hydroxyl groups and C-H bond vibrations; note that some of these bands are negative and others are positive, as discussed further below) and 2000 – 1400 cm<sup>-1</sup> (a region associated with C-O vibrations in formic acid and formate species); in each set of spectra, there are also small bands in the region 3000 – 2600 cm<sup>-1</sup>

and expanded versions of the spectra in this region are also given for clarity. Table 2 summarizes the vibration frequencies and the attribution of the bands observed; details of these attributions will be discussed further below as appropriate.

### 3.3.1 Interaction of HCOOH with the Pd/SiO<sub>2</sub> catalyst

Figure 2 shows the main IR bands observed when HCOOH was introduced to the unpromoted Pd/SiO<sub>2</sub> sample at 333 K as well as the behavior of these bands after the sample had been heated to 453 K after substituting the flow of HCOOH/He by pure He. In the spectral region from 4000 to 2800 cm<sup>-1</sup>, a negative band occurs at ca 3740 cm<sup>-1</sup> following admission of HCOOH at 333 K and this is accompanied by a broad positive band centered at about 3200 cm<sup>-1</sup> and a sharp band at 2938 cm<sup>-1</sup>. On removing the HCOOH at 333 K, each of these bands decreases and almost disappears on heating to temperatures of 393 K and above. As shown more clearly in the expanded spectrum in the region 3000 – 2600 cm<sup>-1</sup>, the sharp band at 2938 cm<sup>-1</sup> formed in the presence of HCOOH is reduced on heating till 453 K without formic acid but it does not disappear completely. The same applies to the band appearing at 1739 cm<sup>-1</sup>. A band is also found at 1578 cm<sup>-1</sup>, but it is very weak.

We attribute the negative band at 3740 cm<sup>-1</sup> to the disappearance of vibrations associated with at least some of the isolated surface OH groups of the silica, these becoming associated by hydrogen bonding to physically adsorbed/condensed HCOOH species after the introduction of the HCOOH. The broad positive band centered at 3200 cm<sup>-1</sup> is characteristic of the vibration of hydrogen bonded OH groups in the support and condensed HCOOH. The previous IR studies [9,13,14] have reported that physically adsorbed/condensed hydrogen-bonded formic acid is generated after the introduction of formic acid to catalysts and this suggestion is consistent with the explanation given here.

The weak band at  $2938\text{ cm}^{-1}$  occurs in the C-H stretching range and can be ascribed to the  $\nu_{\text{CH}}$  vibration of condensed HCOOH molecules. The band with high intensity visible at  $1739\text{ cm}^{-1}$  is probably due to the C=O stretching mode of HCOOH condensed on SiO<sub>2</sub> while the weak and broad band at  $1578\text{ cm}^{-1}$  is probably due to the asymmetric stretching vibration of a formate species present in a very small concentrations. The bands of gas phase formic acid at about  $1790\text{ cm}^{-1}$  contribute negligibly to the band of condensed formic acid at  $1739\text{ cm}^{-1}$  as a shoulder on the left hand side.

The second set of spectra of Figure 2 show that the bands at  $1739\text{ cm}^{-1}$  and  $2943\text{ cm}^{-1}$  as well as the broad band centered at  $3200\text{ cm}^{-1}$  all decreased after switching off the HCOOH flow and replacing it by a flow of pure He at 333 K. This result indicates that gas phase HCOOH is in equilibrium with condensed HCOOH over the Pd/SiO<sub>2</sub> catalyst. Further desorption of condensed HCOOH took place with an increase in temperature (top two spectra); however, the band at  $1739\text{ cm}^{-1}$  still remained even at a temperature as high as 453 K, this band being ascribed to a C=O vibration. Both the negative band at  $3740\text{ cm}^{-1}$  and the broad band centered at  $3200\text{ cm}^{-1}$  disappeared with the increase in temperature, this indicating that the desorption of HCOOH freed up the isolated hydroxyl groups on the silica support.

### **3.3.2 Interaction of HCOOH with the 4K-Pd/SiO<sub>2</sub> catalyst**

The interaction of HCOOH with a sample of the K-doped Pd/SiO<sub>2</sub> catalyst was carried out following the same procedure as that used for the undoped Pd/SiO<sub>2</sub> sample and the results are shown in Figure 3. As with the spectra obtained for Pd/SiO<sub>2</sub> (Figure 2), introduction of HCOOH to the 4:1 K-Pd/SiO<sub>2</sub> catalyst at 333 K gave rise to a sharp negative band at  $3740\text{ cm}^{-1}$  due to the transformation of isolated hydroxyl groups to hydrogen bonded species as well as to a broad positive band at  $3300\text{ cm}^{-1}$  due to the OH

vibration in the hydrogen bonded hydroxyl groups of condensed HCOOH and of silica, both bands increasing slightly with time (not shown in the figure).

The intensities of both the bands ascribed to the condensed HCOOH (2937 and 1740  $\text{cm}^{-1}$ ) were lower than those observed with the undoped Pd/SiO<sub>2</sub>. The most significant difference between the unpromoted and K-promoted samples is seen in the region 2000 – 1400  $\text{cm}^{-1}$  with the appearance, in addition to the band at 1740  $\text{cm}^{-1}$ , of a strong absorption at 1586  $\text{cm}^{-1}$  characteristic of an asymmetric OCO vibration of formate species. This band appears to be due to the presence of formate ions in a solution of potassium formate in formic acid or water [8]. This observation confirms the formation of formate anions on the K-promoted catalyst, showing that quite a considerable proportion of the adsorbed HCOOH dissociates into formate anions over the K-Pd/SiO<sub>2</sub> sample at 333 K in contrast to the undoped sample (Figure 2).

Figure 3 also shows spectra taken after switching from the flow containing HCOOH to pure He at 333 K and increasing the temperature to 493 K. The C=O vibration band at 1740  $\text{cm}^{-1}$  due to condensed HCOOH disappeared totally at 393 K and this contrasting with the result obtained with the undoped Pd/SiO<sub>2</sub> catalyst with which a small band was still found after heating to 453 K (Figure 2). Both the negative band at 3740  $\text{cm}^{-1}$  and the broad band centered at 3300  $\text{cm}^{-1}$  disappeared with increasing temperature. However, the formate band at 1586  $\text{cm}^{-1}$  discussed above shifted from 1586  $\text{cm}^{-1}$  to 1606  $\text{cm}^{-1}$ , growing slightly in magnitude, after switching from the HCOOH to pure He on heating to 393 K; this band decreased slightly in magnitude once more on heating the sample further to 493 K.

Three bands, at 2916  $\text{cm}^{-1}$ , 2822  $\text{cm}^{-1}$  and 2726  $\text{cm}^{-1}$ , all corresponding to C-H stretching frequencies, appeared at 333 K on switching to He in place of the single band

at  $2937\text{ cm}^{-1}$ . (The additional two bands may have been present with formic acid but, if so, were very indistinct.) The band at  $2937\text{ cm}^{-1}$  found in the presence of formic acid is probably a combination of bands due to C-H stretching in the condensed HCOOH species as well as in formate species; this band attenuated and shifted to  $2916$  after removing the HCOOH from the feed gas. As noted above for the band occurring at about  $1606\text{ cm}^{-1}$ , these additional bands shifted to  $2809\text{ cm}^{-1}$  and  $2700\text{ cm}^{-1}$  when the temperature was increased to  $393\text{ K}$ .

These changes brought about by switching from a flow containing HCOOH to one of pure He and heating is possibly due to the appearance of another form of formate species in addition to formate anion ( $1585\text{ cm}^{-1}$ ) existing in a solution of KHCOO [8]. The band at  $1606\text{ cm}^{-1}$  could be assigned to “bulk” formate (crystalline or molten KHCOO). The bulk formate provides more intense C-H stretching bands compared to those given by formate anions in solution. The bulk formate band at  $1606\text{ cm}^{-1}$  is still observed in the spectrum at  $493\text{ K}$  indicating high stability and low reactivity of this formate. The disappearance of the bands associated with condensed HCOOH at lower temperatures in the case of the K-doped sample than in the case of the undoped material would appear to be due to its involvement in the decomposition reaction and by the much higher reactivity of the doped catalyst (Figure 1).

### **3.3.3 HCOOH decomposition at different temperatures over the 4K-Pd/SiO<sub>2</sub> catalyst**

Figure 4 shows equivalent DRIFTS results to those shown in Figure 3 for the 4K-Pd/SiO<sub>2</sub> catalyst but in which formic acid was not removed from the gas flow when the temperature was raised. The bands at  $2934\text{ cm}^{-1}$  and  $1740\text{ cm}^{-1}$ , both of which are

characteristic of condensed HCOOH, decreased with increasing temperature, this confirming the existence of an equilibrium with gas phase HCOOH. These bands are still observed at 393 K in contrast to the data for heating in He (Figure 3). The bands assigned to formate anions and bulk formate species increase with temperature.

## 4. Discussion

The DRIFT spectra obtained during the HCOOH interaction with the K-promoted Pd/SiO<sub>2</sub> catalyst studied here show typical strong bands due to the C=O stretching frequencies of condensed formic acid together with broad bands attributable to OH species in condensed HCOOH and support OH species hydrogen bonded to HCOOH. The results above show that a significant proportion of the HCOOH introduced is condensed on the catalysts, this being consistent with the results published by the other research groups [9,13,14] and with the non-steady state results presented in our previous paper [6]. We concluded from the latter results that a considerable fraction of the HCOOH introduced to a fresh K-promoted catalyst is condensed in the pores of the catalyst (Figure 5a) and that formate anions stabilized by K ions in solution are also formed.

It is notable that the peaks attributed to formate species became even stronger after switching from HCOOH to He and that some of the bands due to formate species were still discernible at temperatures as high as 493 K. It can be suggested that two different states of the formate species exist: mobile formate anions present in liquid HCOOH; and bulk potassium formate species formed after most of the HCOOH is desorbed from the catalyst pores (Figure 5b) or present even in the condensed liquid if potassium content is taken in excess. The bands of typical OCO stretching vibration of formate shifted from 1586 cm<sup>-1</sup> to 1606 cm<sup>-1</sup> after switching from HCOOH in He to pure He and heating

showing that there was a change in the form of the formate species during this process. The existence of a stable bulk formate at 493 K implied that it dissociates less easily and has decreased mobility over the surface in the absence of condensed HCOOH.

The introduction of K into Pd based catalysts on different supports significantly accelerates the decomposition of formic acid. The promoted reaction steps were represented in the Figure 6. In the first step, a phase consisting of liquid formic acid is formed within the pores of the catalyst and this phase then provides a reservoir for the formation of formate anions with participation of  $K^+$  ions. The formate anions then decompose to form  $CO_2$  and give gaseous hydrogen via hydrogen species on the Pd surface. In the liquid condensed in the pores, bulk potassium formate (crystalline or molten) exists in equilibrium with formate ions and  $K^+$ . In our previous publication [6], we speculated on the importance of the liquid phase for the catalytic promotional effect as depicted in Figure 6; this is clearly confirmed by the DRIFTS results here. The concentration of formate ions present in aqueous formic acid is negligible because of its low dissociation constant. However, the presence of alkali metal ions completely changes this situation, giving a significant concentration of formate ions in a buffer-like solution consisting of formate anions, K ions, protons and HCOOH explained by our previous work [6].

The dissociation of formate ions to give adsorbed hydrogen on Pd and forming gaseous  $CO_2$  appears to be the rate determining step in the all-over reaction as the reaction rate is dependent on the concentration of  $K^+$  ions, this determining the concentration of formate ions [6]. In the experiments reported here, after switching from the HCOOH-containing flow to pure He, bulk formate crystallized in the pores from the decreasing volume of liquid HCOOH (Figure 5b) and was stable at the high temperature of 493 K.

The liquid formic acid when present provides easy access of the formate anions to all the surface Pd sites.

The presence of water is inevitable in the reaction system as it could either be formed as a side product of formic acid dehydration (with CO and water as products) or be introduced to the system during the transformation of the potassium carbonate used for impregnation into potassium formate via reaction (4):



The change of the standard pressure Gibbs free energy for this reaction is  $-98 \text{ kJ mol}^{-1}$  at 343 K. Thermal conversion of formates to carbonates in inert atmosphere normally takes place at temperatures higher than those used for the performed DRIFTS study [15]. This explains why carbonates are not observed in our conditions.

The introduction of extra water (2.5 vol.%) into the reactant flow did not have a significant influence on the DRIFT spectra obtained for the K-doped catalyst (see Figure S1, Supplementary information file); nor were substantial changes observed during the non-steady state period (see Figure S2). Balarew et al. [16] showed that potassium formate can be nicely dissolved in both formic acid or water. The final step in the reaction scheme is the recombination of two atoms of hydrogen adsorbed on the Pd active sites to produce gaseous hydrogen. This step is reversible.

## 5. Conclusions

It can be concluded that the addition of potassium to a Pd/C catalyst has a remarkable promotional effect on the catalytic activity and hydrogen selectivity for formic acid decomposition, the reaction rate being increased by 1-2 orders of magnitude. Having



shown that similar promotional effects were exhibited by K-doped Pd/SiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> materials, DRIFT spectra of the interaction of HCOOH with Pd catalysts supported on silica were obtained to provide a greater understanding of the intermediate species participating in the reaction. The DRIFTS results demonstrate that a considerable amount of HCOOH was condensed on the catalyst and the presence of potassium over doped catalyst contributed to the formation of a buffer-like solution, this giving rise to the high concentration of formate ions in the reaction system. The DRIFTS results confirmed that the liquid phase of HCOOH and mobile formate ions are two essential features with respect to the promotion of the catalysts by providing formate ions to the Pd sites.

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## **Appendix A. Supplementary data**

Supplementary data associated with this article can be found in the online version, at

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## Figure Captions

**Figure 1:** Temperature dependence of conversion (a) and hydrogen selectivity (b) in the formic acid decomposition over undoped catalysts, Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/SiO<sub>2</sub>, Pd/C, and doped catalysts, 2:1 K-Pd/Al<sub>2</sub>O<sub>3</sub>, 4:1 K-Pd/SiO<sub>2</sub>, 10:1 K-Pd/C.

**Figure 2:** DRIFT spectra of the Pd/SiO<sub>2</sub> catalyst in HCOOH at 333 K and in He at different temperatures.

**Figure 3:** DRIFT spectra of the 4:1 K-Pd/SiO<sub>2</sub> catalyst in HCOOH at 333 K and in He at different temperatures.

**Figure 4:** DRIFT spectra of the 4:1 K-Pd/SiO<sub>2</sub> catalyst in HCOOH at different temperatures.

**Figure 5:** Schematic representation of the K doped catalyst (a) in HCOOH and (b) in He (Pd particles are not shown).

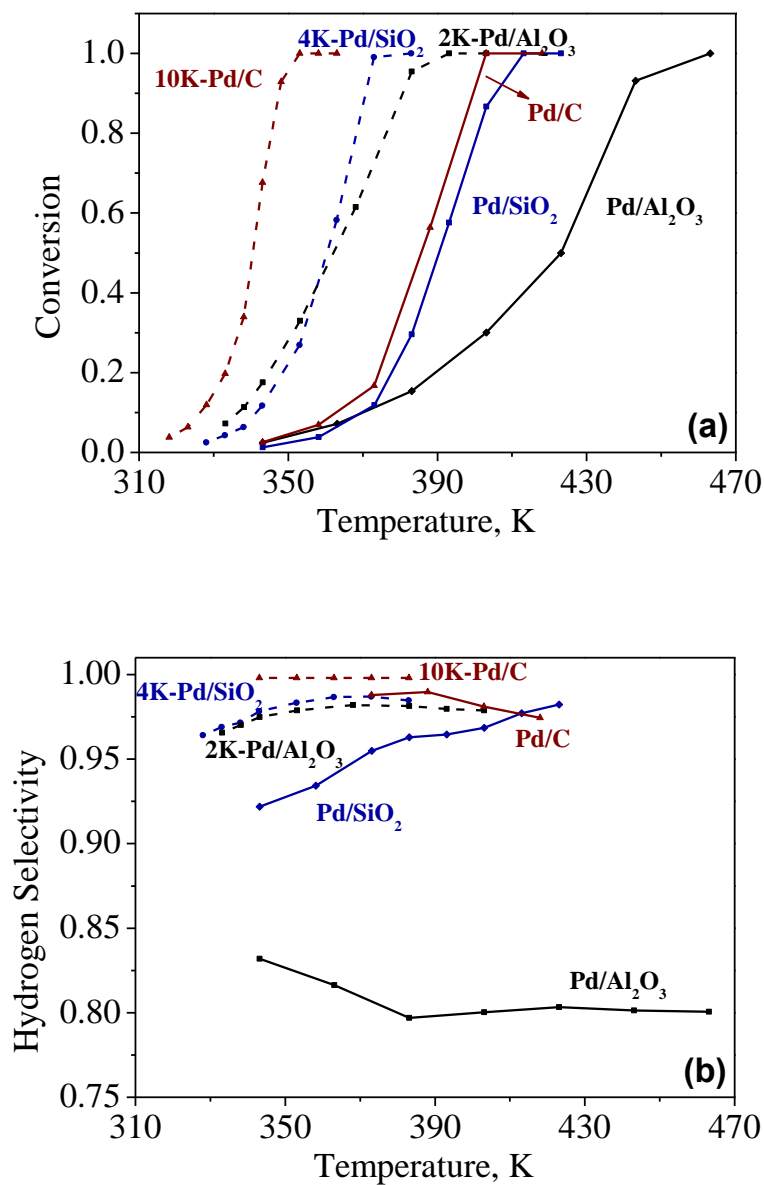
**Figure 6:** Schematic representation of the mechanism of the formic acid decomposition on Pd catalysts doped with potassium ions. The characteristic IR bands positions are indicated.

**Table 1:** Characteristics and kinetic data for the catalysts studied

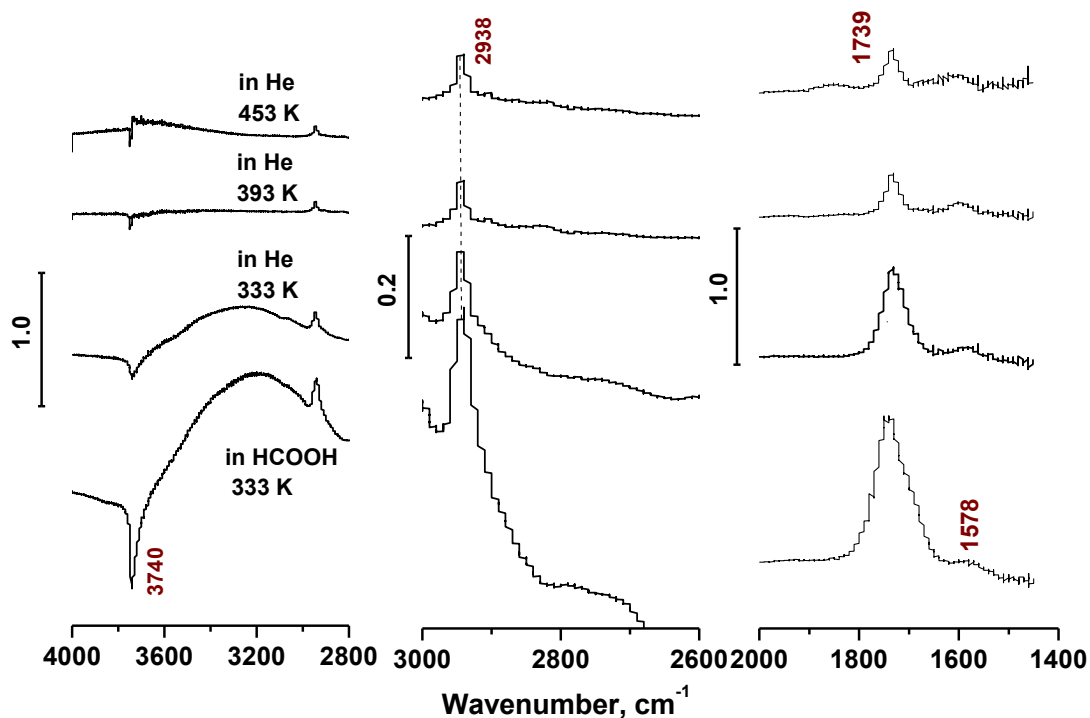
Catalysts	BET surface area, m <sup>2</sup> g <sup>-1</sup>	Mean particle size, nm	TOF at 343 K, s <sup>-1</sup>	Activation energy, kJ mol <sup>-1</sup>
1 wt.% Pd/C	933	3.6 ± 1.7	0.008	65
10:1 K- Pd/C	688	3.7 ± 1.3	0.27	97
1 wt.% Pd/SiO <sub>2</sub>	380	7.4 ± 2.4	0.0095	78
4:1 K- Pd/SiO <sub>2</sub>	/	/	0.079	95
1 wt.% Pd/Al <sub>2</sub> O <sub>3</sub>	144	4.2 ± 1.0	0.010	49
2:1 K- Pd/ Al <sub>2</sub> O <sub>3</sub>	/	/	0.075	84

**Table 2:** Summary of the major vibration frequencies (in cm<sup>-1</sup>) observed following interaction of the catalysts with HCOOH

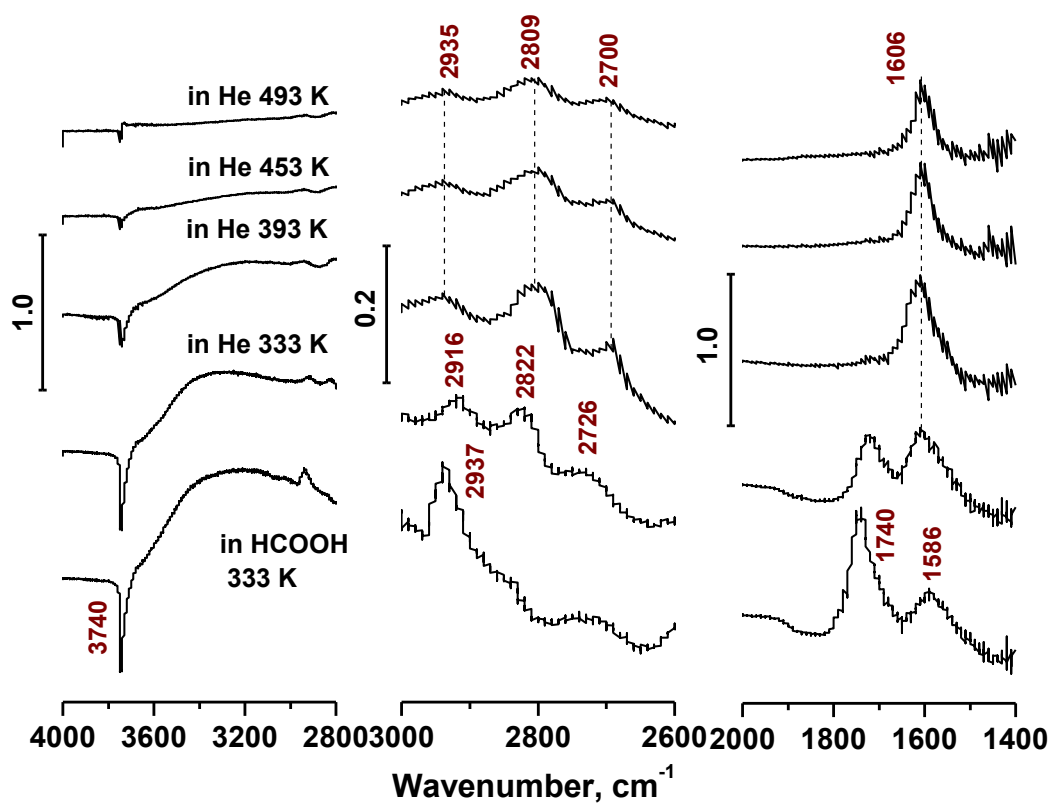
Assignment	Pd/SiO <sub>2</sub>	4:1 K-Pd/SiO <sub>2</sub>
v(C=O) formic acid (liquid)	1739	1729-1742
v(CH) formic acid (liquid)	2938	2935
v <sub>as</sub> (OCO) formate ions	1578 (very weak)	1580-1590
v <sub>as</sub> (OCO) bulk formate	Very weak	1606-1611
v(CH) mainly bulk formate	Not found	2822, 2809
2δ(CH) mainly bulk formate	Not found	2716, 2700



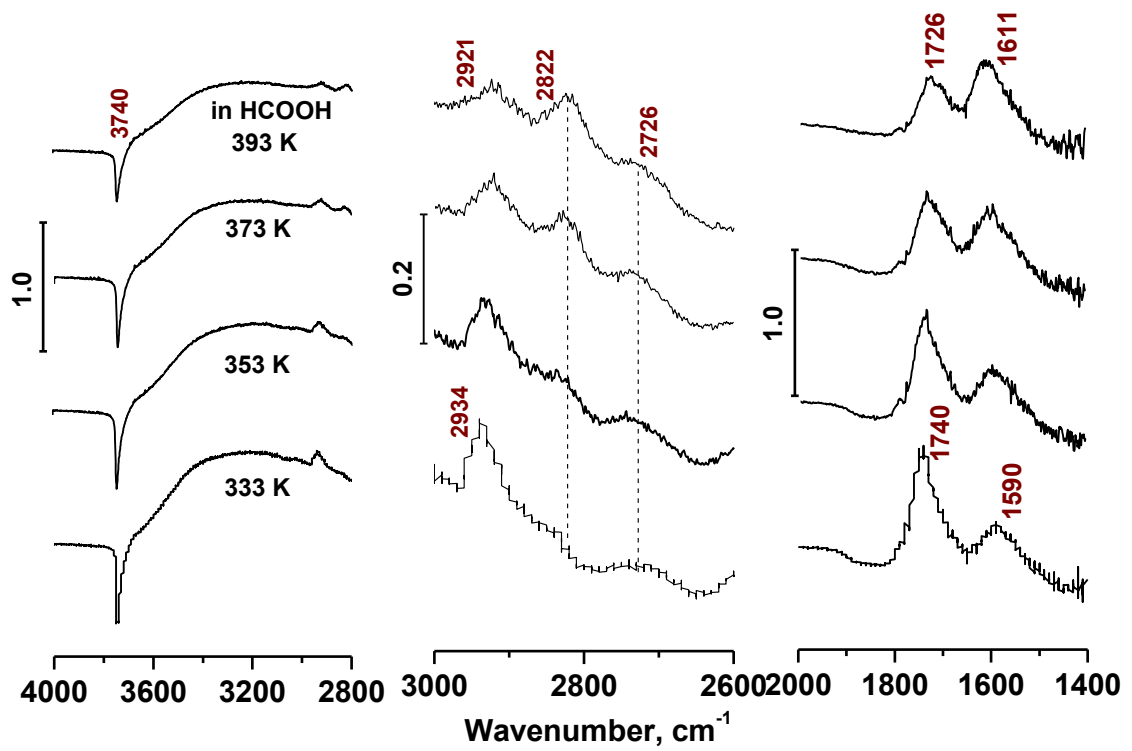
**Figure 1:** Temperature dependence of conversion (a) and hydrogen selectivity (b) in the formic acid decomposition over undoped catalysts, Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/SiO<sub>2</sub>, Pd/C, and doped catalysts, 2:1 K-Pd/Al<sub>2</sub>O<sub>3</sub>, 4:1 K-Pd/SiO<sub>2</sub>, 10:1 K-Pd/C



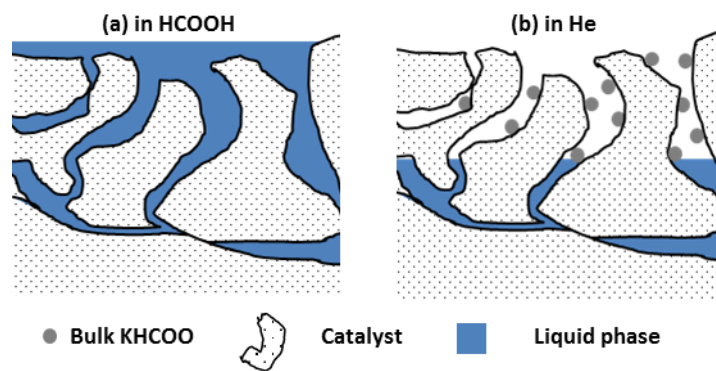
**Figure 2:** DRIFT spectra of the Pd/SiO<sub>2</sub> catalyst in HCOOH at 333 K and in He at different temperatures



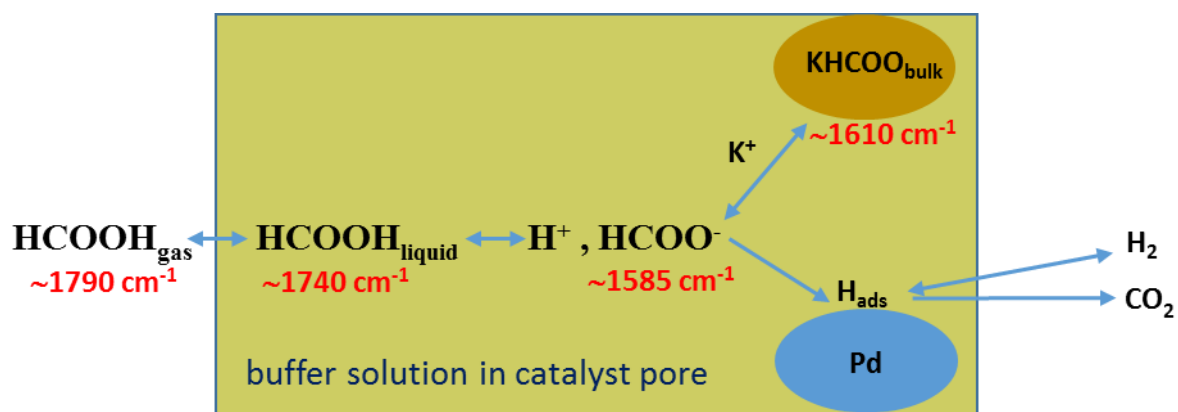
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**Figure 5:** Schematic representation of the K doped catalyst (a) in HCOOH and (b) in He (Pd particles are not shown)



**Figure 6:** Schematic representation of the mechanism of the formic acid decomposition on Pd catalysts doped with potassium ions. The characteristic IR bands positions are indicated