

**Hydrogenation of sunflower oil over Pt-Ni bimetallic supported catalysts:
Preparation, characterisation and catalytic activity**

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Abstract

It had been reported that in order to improve oil hydrogenation catalysts the geometric or electronic effects of the catalysts must be manipulated in order to achieve the desired activity or selectivity. To achieve this, the development of an active and selective bimetallic catalyst was undertaken. An innovative approach was taken to synthesize Pt-Ni catalysts supported on mesoporous silica using the surface redox reaction (Srr) technique. It was determined that the Srr preparation method resulted in better activity and lower selectivity towards *trans* than the traditional successive and co-impregnation bimetallic impregnation techniques. The change in selectivity can be explained by a promoter electronic effect generated by the close proximity of a second metal on the catalysts surface and from a geometric effect due to the incorporation of the Ni on the surface. All the bimetallic catalysts showed a drop in the formation of *trans* compared to the monometallic catalyst.

Keywords: Pt-Ni supported on silica, hydrogenation of sunflower oil, *trans* fatty acids, bimetallic catalysts

1. Introduction

The field of catalytic hydrogenation of edible oil has seen a lot of advances in recent years, especially regarding efforts to reduce the formation of *trans* fats. These *trans* fats are associated with increased risk of coronary heart disease. Researchers have investigated the use of different metals, mainly noble metals, to improve the activity and selectivity of the process [2-8]. Manipulation of the catalytic structure has also been studied in an effort to achieve tighter control of the reaction [9,10]. It has been found that, with some exceptions, the variations of properties achieved on different supports are not as notable as the differences among the metals themselves [a,b]. In order to further promote the selectivity toward C_{18:1} *cis*, noble metals have been modified by the addition of amines in the reaction medium and by metal additives. The influence of these additives has shown increased selectivity to *cis* isomers and in some cases without loss of activity for various hydrogenation reactions [6,11,12].

Rubin et al. [13] presented one of the first studies using a mixed system containing Ni and methyl benzoate chromium tricarbonyl for edible oil hydrogenation. They showed it was possible to retain the advantages of both catalytic metals while using them in combination. Adding Ni to Ru resulted in improved activity and relatively low *trans* isomer formation. At an I.V. of 60 only 7% *trans* isomers were formed (110°C, 57.2 bar, 580 rpm). However, Ru is oil soluble and is difficult to recover at the end of hydrogenation. In addition the operating conditions required relatively high hydrogen pressure (57.2 bar).

The catalytic properties of alloys usually deviate from the additive properties of the metal components. This catalytic phenomenon can be sometimes understood in terms of the so-called ligand (electronic) effect in which unanticipated catalytic properties are the result of a change in the electron structure of the catalyst. It has been widely proposed that the d electrons of a metal play an important role in determining catalytic activity [15]. By varying the composition of the alloy, the degree to which the d band is filled with electrons and the effect it has on the catalytic properties can be observed. While an electronic effect has been used to explain the influence on the selectivity and activity of bimetallic catalysts, the ensemble (geometric) effect at a surface may also play a crucial role in changing catalytic characteristics. Here, the second metal may block sites on the surface of an active metal, and, by that means the average size and composition of the ensemble of active sites is varied [17]. It is also recognized that a combination of electronic and geometric effects can explain the catalytic behavior of some bimetallic systems [16-19].

In studies by Nohair et al. [5,6] the modification of Pd/SiO₂ by the addition of Pb via surface redox reaction (Srr) improved the selectivity to *cis* C_{18:1}, with a small decrease in conversion. Fernández et al. [22] prepared Pd-Me/Al₂O₃ catalysts where Me = molybdenum (Mo), Vanadium (V) and Lead (Pb). All the catalysts were prepared using successive impregnation (S-i). It was shown that the Pd-Mo/Al₂O₃ and Pd-V/Al₂O₃ catalysts presented the same activity as that of the respective monometallic Pd/Al₂O₃ catalyst, but an increased selectivity to *trans*-isomers. The Pd-Pb/Al₂O₃ catalyst showed a low hydrogenation activity. This drop in activity was thought to be a result of certain

dimensional limitations on the space lattice of Pd for hydrogenation of double bonds due to the formation of a Pd-Pb alloy. Wright *et al.* explored the use of homogeneous and heterogeneous bimetallic systems for hydrogenation of vegetable oils [14,23]. They concluded that there was no advantage in combining Pd and MeBeCr(CO)₃. The homogeneous catalyst inhibited the activity of Pd and a high level of *trans* isomers were formed. The addition of Ni to Pd was more promising, resulting in increased catalyst activity but no significant difference in *cis*-selectivity was observed. It was postulated that poison adsorption by the Ni on the Ni-Pd catalyst accounted for the increase in activity.

Encouraged by these reported results, this work examines the hydrogenation of sunflower oil using Pt/SiO₂ catalysts promoted with Ni. The study investigates the dependence of activity and selectivity on the support characteristics, the bimetal preparation and metal precursors. The main objective is to develop a catalyst that is active while lowering the *trans*-isomer content in the hydrogenated oil.

2. Experimental

2.1 Catalysts preparation

The mesoporous silica material, (CNS SiO₂), was synthesised according to a procedure reported in the literature [c]. The resulting solid was calcined at 650°C (ramp rate 1°C min⁻¹) for 6 hours under a stream of air (100 ml min⁻¹). The supported bimetallic catalysts were prepared using the prepared SiO₂ support following three different methods; i) co-impregnation, ii) successive impregnation and iii) surface redox reaction.

i) Co-impregnation (Co-i): The desired amount of precursor metal salt, $\text{Pt}(\text{AcAc})_2$ (Sigma-Aldrich) and $\text{Ni}(\text{NO}_3)_2$ (Sigma-Aldrich), was dissolved in 50 ml ethanol and 1g SiO_2 support added. This suspension was stirred for 10 hours, after which the solvent was removed under vacuum. The sample was then dried overnight at 80°C and finally calcined in air at 450°C for 5 hours.

ii) Successive impregnation (S-i): The desired amount of platinum ($\text{Pt}(\text{AcAc})_2$) was dissolved in 50ml ethanol and 1g of the support (SiO_2) was then added. After stirring, the sample was dried and calcined as described above. The second metal, nickel, was then impregnated using the precursor $\text{Ni}(\text{NO}_3)_2$. The desired amount of the Ni salt, dissolved in 50 ml ethanol, was deposited onto 1g of the supported Pt/ SiO_2 catalyst. This solution was allowed to stir for 10 hours before the solvent was removed and subsequently dried. Finally the solid was calcined in air at 450°C for 5 hours.

iii) Surface redox reaction (Srr): This preparation method, based on a procedure reported by Nohair et al. [5], is known to induce a strong interaction between two metals. Initially, the monometallic Pt/ SiO_2 catalyst was synthesized by wet-impregnation, as described above. This calcined monometallic catalyst was then introduced into a reactor under argon and was activated under hydrogen at 200°C for 4 hours. A degassed solution of the modifier precursor $\text{Ni}(\text{NO}_3)_2$ in 50 ml methanol was then introduced onto the catalyst at room temperature. The suspension was stirred and maintained under a H_2 flow for 90 minutes. The solution was then filtered and dried overnight at 80°C .

2.2 Hydrogenation of sunflower oil

The hydrogenation of sunflower oil (Flora) was carried out in a batch reactor at 170°C under 3 bar hydrogen pressure, using 150mg catalyst per 100ml oil in a procedure described elsewhere [b]. Oil samples were taken from the reactor every hour and the entire reaction time was 5 hours. The oil samples were analysed for its iodine value (IV) according to EN ISO 3961 Wijs method [26]. The iodine value of an oil or fat is a measure of unsaturation and was used to monitor the activity of the catalysts. The fatty acid composition of the hydrogenated oils was determined by gas chromatography (GC) using a procedure described elsewhere [b].

2.3 Catalyst Characterisation

XRD patterns were obtained using a Philips X'Pert Pro X-ray diffractometer with nickel filtered K_{α} Cu radiation ($\lambda = 1.542 \text{ \AA}$) between the C-ray source angles of 10° and 70°. The specific surface area measurements and the pore size distributions of the catalytic materials were determined from N₂ adsorption/desorption experiments at -196°C using a Micrometrics ASAP 2010 system. The pore volume and pore size distribution were calculated using the Barrett-Joyner-Halenda theory from the adsorption isotherm. A Varian SpectrAA Atomic Absorption Spectrometer was used to measure the Pt and Ni contents of the prepared catalysts. The metal dispersion and average particle size was measured using a dynamic pulse technique described elsewhere [b]. A Jeol 2011 Transmission electron microscope was used to obtain high resolution images of the different catalysts. The imaging programme, Digital MicrographTM, was used to visualise

and analyse digital image data from the electron microscope. The software was to calculate the average metal particle size by sampling at least 100 particles.

3. Results and Discussion

3.1 Promotional effects of Ni on Pt catalysts using different preparation methods

Table 1 presents the textural properties and metal loading of the SiO₂ support, the monometallic Pt/SiO₂ catalyst and a series of supported bimetallic Pt-Ni catalysts. The nomenclature of the catalysts includes the measured amount of metal supported onto the SiO₂ and the preparation method used (co-impregnation (Co-i), successive impregnation (S-i) and surface redox reaction (Srr)). The 1.57%Pt-0.72%Ni/SiO₂ (S-i) catalyst was prepared by successive impregnation where the Pt metal was loaded on first and then the Ni. Correspondingly the 0.83%Ni-1.37%Pt/SiO₂ (S-i) was prepared using successive impregnation but the Ni was added first.

The B.E.T. analysis of the silica support showed a specific surface area of 601 m²g⁻¹, while the impregnated Pt/SiO₂ catalyst presented a surface area of 541 m²g⁻¹. The average pore diameter of the support was found to be 18.9 nm, signifying mesoporous characteristics. The slight decrease in pore diameter and pore volume for the 1.57% Pt/SiO₂ in comparison to the support may indicate that minor sintering of the support have occurred due to the recalcination step or some of the metal particles have blocked a fraction of the pores.

The co-impregnated and successive impregnated catalysts showed the largest decrease in surface area compared to the original support. This may indicate that the metal particles were blocking a fraction of the pores of the support. In the case of the catalysts prepared by successive impregnation, the recalcination stage may have affected the textural properties in that, it may have led to sintering of the pores. Not only was the surface area lower but the average pore diameter was also found to have decreased compared to the other methods of preparation.

Table 1: Support and catalyst properties

Catalyst name	Specific surface area (m^2g^{-1})	Pore diameter (nm)	Pore volume (cm^3g^{-1})	Actual Pt metal loading (%)	Actual Ni metal loading (%)
SiO ₂	601	18.9	1.53		
1.57%Pt/SiO ₂	541	18.4	1.41	1.57	
1.16%Pt-0.41%Ni/SiO ₂ (Co-i)	467	18.4	1.30	1.16	0.41
1.57%Pt-0.72%Ni/SiO ₂ (S-i)	431	15.6	1.08	1.57	0.72
0.83%Ni-1.37%Pt/SiO ₂ (S-i)	443	16.1	1.11	1.37	0.83
1.56%Pt-0.95%Ni/SiO ₂ (Srr)	518	17.9	1.37	1.56	0.95

Table 2 presents the average particle sizes, using two different techniques, and the % dispersion for the prepared catalysts. Dispersions for the bimetallic catalysts range from 4.4 to 7.2% based on total H₂ uptake. For the monometallic 1.57%Pt/SiO₂ catalyst, H₂ chemisorption revealed the Pt metal dispersion was 41% and Pt particle sizes averaging 2.8 nm. This correlates well with published data [29,30].

The average particle size calculated from the chemisorption correlates with the TEM particle size for all the catalysts, except for the 1.56%Pt-0.95%Ni/SiO₂ (Srr) catalyst. Large metal particles were formed when Pt and Ni were prepared by co-impregnation.

The addition of the Ni with the Pt metal together may have resulted in the reduced dispersion and increase in overall particle size. Malyala et al. [31] reported that segregates of Ni particles of different sizes (21-35 nm) and shapes are formed by wet impregnation, leading to a lower degree of dispersion. The large particles present on the catalysts prepared by successive impregnation could have arisen because of the recalcination step. A decrease in the interfacial energy at the metal-oxide/support interface allows the metal particles to freely move and aggregate. This metal re-dispersion and agglomeration is well documented in the literature [18,32,33].

Table 2: Dispersion and average particle size for prepared catalysts

Catalyst name	Dispersion (%)	H ₂ chemisorption Particle size (nm)	TEM Particle size [†] (nm)
1.16%Pt-0.41%Ni/SiO ₂ (Co-i)	7.2	16.1	17.8
1.57%Pt-0.72%Ni/SiO ₂ (S-i)	6.3	18.4	17.1
0.83%Ni-1.37%Pt/SiO ₂ (S-i)	5.9	20.6	21.7
1.56%Pt-0.95%Ni/SiO ₂ (Srr)	4.4	26.3	7.9
1.57%Pt/SiO ₂	41	2.8	3.0

[†]Number-average particle size. Determined by counting a minimum of 100 free standing particles.

All the catalysts were tested for the hydrogenation of sunflower oil. The hydrogenation activity was monitored by the decay of Iodine Value (IV), while the GC results show the change in the fatty acid compositions over hydrogenation time. Figure 1 shows the drop in IV for the indicated catalysts over time. The 1.57%Pt/SiO₂ monometallic catalyst showed the highest activity of all the catalysts tested reaching an IV of 51 after 5 hours. Comparatively, the bimetallic catalysts were less active following the addition of Ni to Pt. The traditional techniques of impregnation (Co and successive) produced the less active catalysts, with 1.16%Pt-0.41%Ni/SiO₂ (Co-i) achieving an IV of 74 after the 5

hours. The 1.57%Pt-0.72%Ni/SiO₂ (S-i) and 0.83%Ni-1.37%Pt/SiO₂ (S-i) achieved IV's of 71 and 69, respectively. The Srr catalyst showed the highest activity of all the bimetallic catalysts, with an IV value of 58 after the 5 hours. These results indicate that the addition of Ni decreases the activity of the Pt catalysts and can be explained by the deposition of less active Ni atoms on the surface of the platinum particles, limiting the accessibility to Pt active sites. The severe inhibition of the catalyst activity by the traditional impregnation methods may indicate a strong interaction between the two metals. Nohair et al. [5,6] explained that the difference in behaviors between the traditional and Srr modes of preparation was due to the selective deposition of nickel on particular sites near the platinum when introduced by catalytic reduction. This would prevent the blocking or covering of the active Pt metal particles.

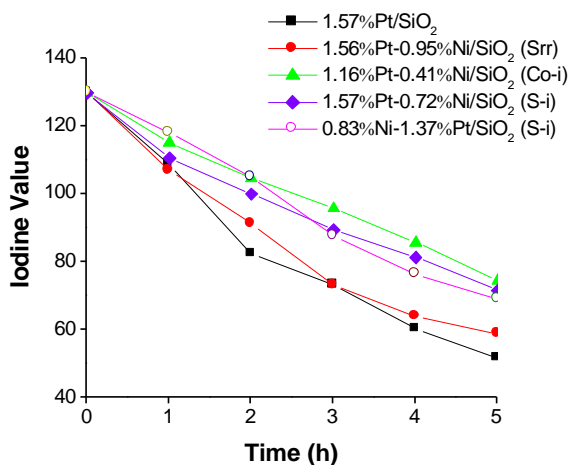


Figure 1: Drop in IV over hydrogenation time for indicated catalysts (170°C, 3 bar H₂, 400 rpm, 100ml oil, 150mg catalyst)

The change in linoleate (C_{18:2}), oleate (C_{18:1cis} and C_{18:1trans}) and stearate (C_{18:0}) components of sunflower oil with time for the mono and bimetallic catalysts are

presented in Figure 2. For all catalysts, the linoleate is consumed, while a steady increase in the $C_{18:1}$ *trans* and stearate content is observed with time. The vertical line indicates the time required to hydrogenate the oil to an iodine value of 70. At this value, the 1.57%Pt/SiO₂ catalyst (figure 2a) presented a *trans* content of 26.5% and a stearate value of 17.8%. The four bimetallic catalysts showed varying results for *trans* formation. At an IV of 70 the co-impregnated bimetallic catalyst formed 23% *trans* (figure 2b). The 1.57%Pt-0.72%Ni/SiO₂ (S-i) and 0.83%Ni-1.37%Pt/SiO₂ (S-i) catalysts produced 23.2% and 18.5% *trans*, respectively. It seems that the order in which the metals are added influence the *trans* selectivity. The amount of metals are present may also affect the formation of the *trans* isomers. The Srr synthesized bimetallic catalyst formed the lowest concentration of *trans* isomers (16.8%) of the four bimetallic catalysts tested. This was a significant drop in the *trans* level compared to the 1.57%Pt/SiO₂ monometallic catalyst.

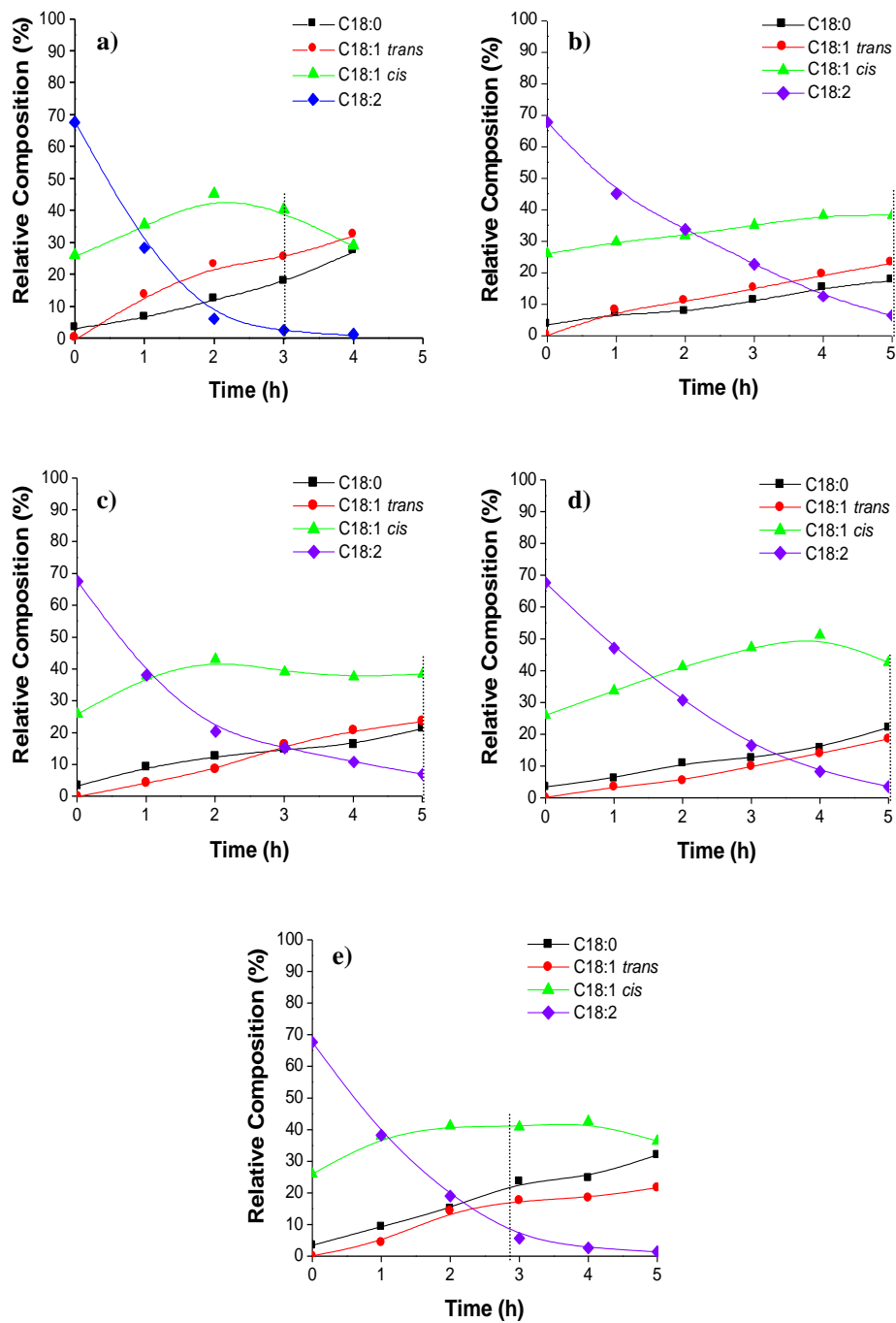


Figure 2: Change of oil composition with time using a) 1.57%Pt/SiO₂, b) 1.16%Pt-0.41%Ni/SiO₂ (Co-

i), c) 1.57%Pt-0.72%Ni/SiO₂(S-i), d) 0.83%Ni-1.37%Pt/SiO₂(S-i) and e) 1.56%Pt-0.95%Ni/SiO₂(Srr) (170°C, 3 bar H₂, 400 rpm, 100 ml oil, 150 mg catalyst)

Figure 3 compares the % stearate and % *trans* at an IV of 70, for all the prepared catalysts. For the same level of conversion (IV of 70) the 1.56%Pt-0.95%Ni/SiO₂ (Srr) catalyst generated the least *trans*-isomers of all catalysts (16.8%). The monometallic 1.57%Pt/SiO₂ catalyst presented the highest level of *trans* but the lowest level of stearate (C_{18:0}) of the tested catalysts. Overall, while the 0.83%Ni-1.37%Pt/SiO₂ (S-i) and the 1.56%Pt-0.95%Ni/SiO₂ (Srr) catalysts generated a lower level of *trans*, this was offset by the higher level of stearate formed, 22% and 23.2%, respectively, at an IV 70.

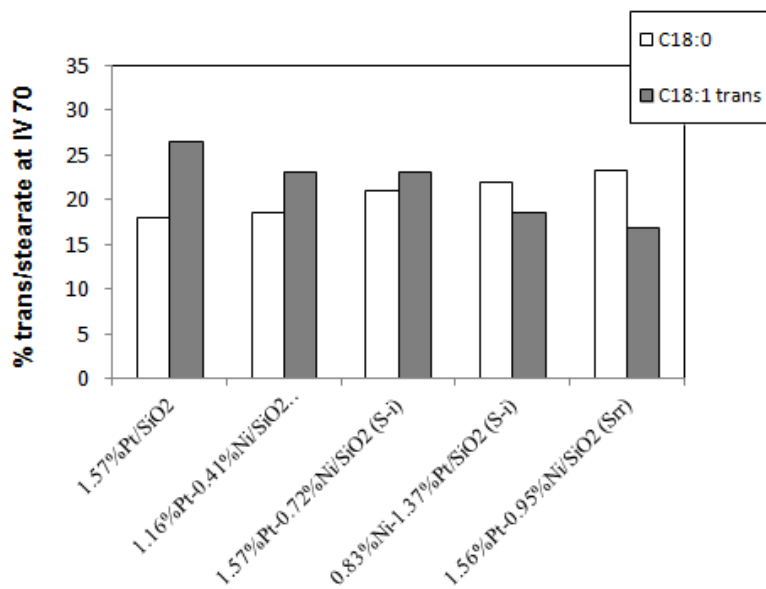


Figure 3: Percentage *trans* and stearate formed at an iodine value of 70 for the indicated catalysts. (170°C, 3 bar H₂, 400 rpm, 100 ml oil)

From these results it is clear that the alloying of Ni with a Pt catalyst and the synthesis method of the bimetallic catalysts have an effect on the hydrogenation process. The

results show that when Ni is deposited onto a Pt catalyst by co-impregnation or successive impregnation the activity is significantly reduced. The surface redox reaction method only slightly inhibits the activity, if at all. This catalyst also showed the best selectivity forming the lowest levels of % *trans* at a comparable IV. Although the 0.83%Ni-1.37%Pt/SiO₂ (S-i) also formed a low level of % *trans*, the 1.56%Pt-0.95%Ni/SiO₂ (Srr) catalyst is seen as a superior catalyst as it not only reduced the % *trans*, it did so without affecting the hydrogenation activity. In an attempt to further understand this phenomenon the bimetallic catalysts were characterized using different techniques.

3.2 Characterization of the surface composition of bimetallic catalysts

Sinfelt [16, 21] reported that the addition of two metals to a support results in a catalyst called a “bimetallic cluster” rather than an alloy, since systems of interest include metallic combinations that do not form alloys in the bulk. To verify this hypothesis a closer look at the surface of the bimetallic Pt-Ni catalysts was carried out to see what form the metals appear.

XRD patterns for the prepared catalysts are shown in Figure 4. Since the crystalline peaks of interest appear in the 2θ range of 30° to 70° , only this section of the diffractogram is shown. The mesoporous SiO₂ is amorphous and does not present a diffractive peak. The classical co-impregnation and successive impregnation techniques all show diffraction peaks primarily associated with the monometallic or monometallic oxide species. This indicates the presence of large segregated particles of Pt and NiO on the catalyst surface. Indeed, TEM and H₂ chemisorption analysis also show that the Pt

and Ni particles are large. A diffractive peak appearing at 35.7° may indicate the presence of cubic $\text{Ni}_{10.25}\text{O}_4\text{Pt}_3(210)$. The presence of this compound could be indicative of the presence of bimetallic oxide particles. The Srr synthesized catalyst and the monometallic Pt/SiO₂ catalyst displayed little or no diffraction peaks. The absence of diffraction peaks indicates the presence of very small particles, which corroborates with the TEM analysis.

Although the dispersion was quite low for the bimetallic 1.56%Pt-0.95%Ni/SiO₂ (Srr) catalyst, the particles were still quite small; hence the lack of sharp diffraction peaks. A discrepancy between TEM and H₂ chemisorption particle size results was already presented in Table 1.

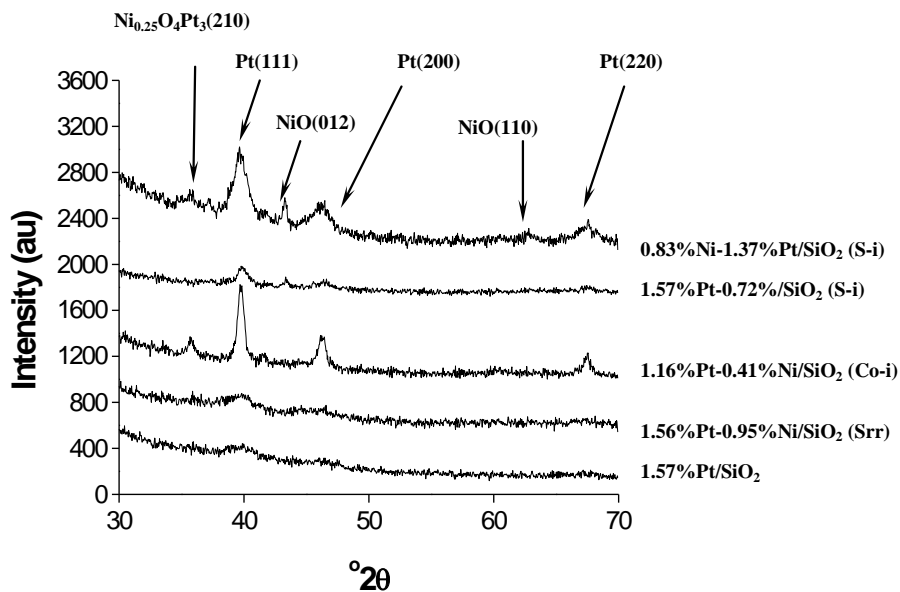


Figure 4: XRD patterns for indicated catalysts

A typical bright field image (BF) of 1.57%Pt/SiO₂ is shown in Figure 5. Good contrast is observed for the Pt particles and individual metal particles can be identified (black spots). Using the DigitalMicrograph™ software it was possible to measure the Pt particle sizes

on the support (3 nm). The images show that the Pt particles are well dispersed on the support, which corroborates well with the H₂ chemisorption dispersion result of 41%.

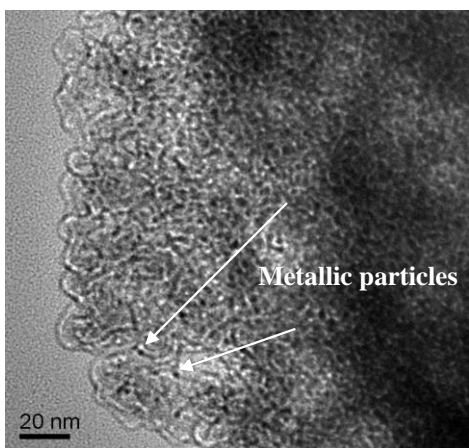


Figure 5: Bright field TEM images of 1.57%Pt/SiO₂

TEM micrographs were taken of each of the bimetallic catalysts and are shown in Figure 6. Both bright field images and the corresponding dark field images are shown for all samples. Dark field imaging (DF) was used in an effort to solely identify the Pt and Ni metal particles. This technique allows for the highest contrast between amorphous and crystalline regions, the crystalline regions reflect, thus appearing extremely bright white, whilst the amorphous regions are darker. As the SiO₂ support is amorphous and metals are generally crystalline, the DF images shown in Figure 6 clearly represents the metal particles on the SiO₂. Metal particle sizes were measured from these images.

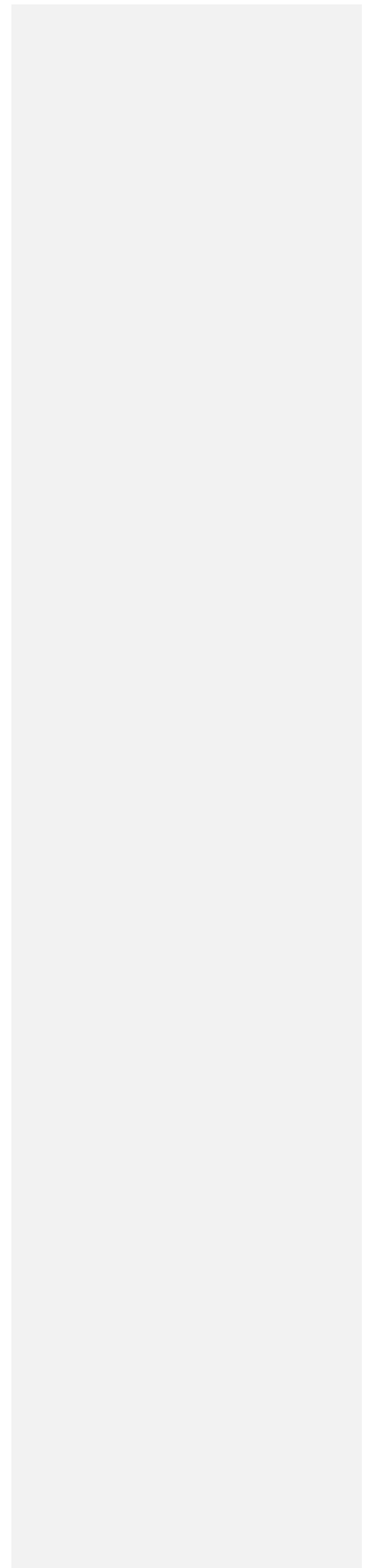
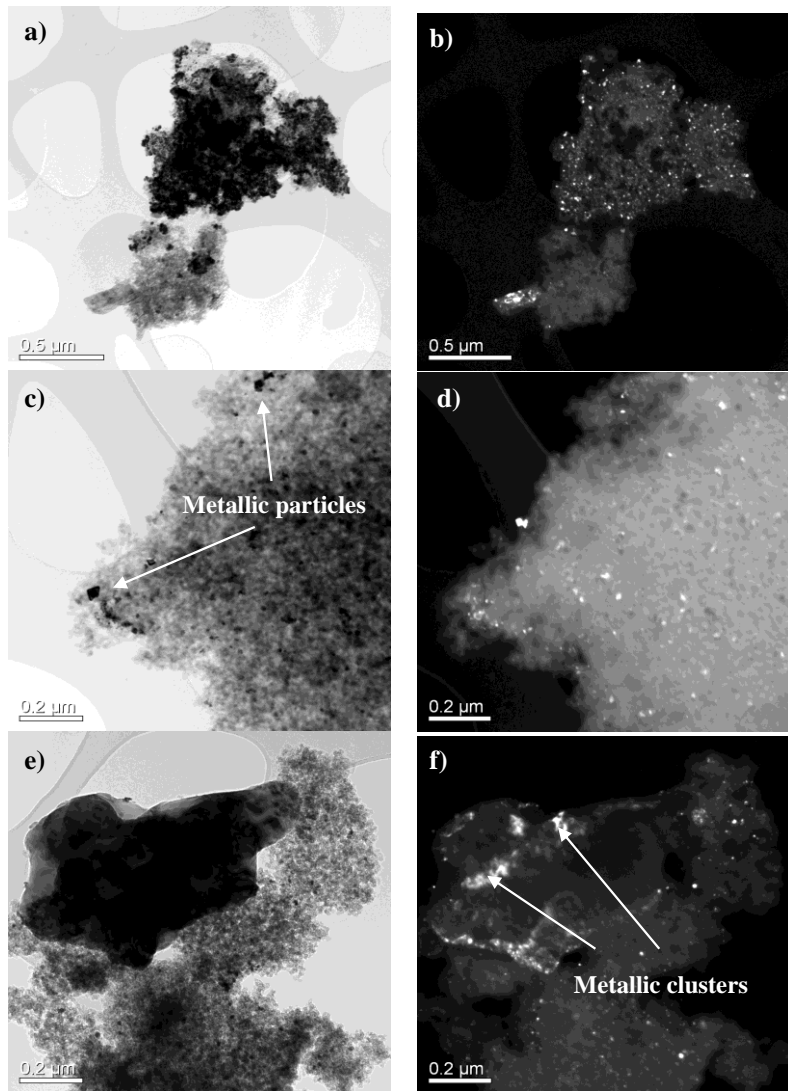
The traditional impregnated catalysts (Figures 6a-f) all showed large metallic particles present on the support surface. The particles observed, both in the BF and DF imaging,

are much larger than those seen on the 1.56%Pt-0.95%Ni/SiO₂ (Srr) catalyst (Figures 6g and h). Interestingly, the DF images show a tendency for the impregnation methods to form metallic clusters [21]. These formations were not seen on the particles tested for the Srr catalyst. Sinfelt [21] put forward the idea that at sufficiently high temperatures the two metals will be completely miscible to explain the presence of these clusters. When the bimetallic co and successive-impregnated catalysts were recalcined at a temperature of 450°C for 5 hours, this temperature may have been high enough for the Pt-Ni to form clusters. The Srr reaction did not involve a recalcination step therefore it is more likely that the individual phase will exist as separate particles.

In Figure 6 g) large dark patches are identifiable for the 1.56%Pt-0.95%Ni/SiO₂ (Srr) catalyst, supporting the low dispersion result of 4.4% obtained by chemisorption. The drop in dispersion from 41% for the 1.57%Pt/SiO₂ catalyst to 4.4% can probably be explained by the sintering of the metal particles during the surface redox reaction treatment in an aqueous medium under hydrogen. This sintering phenomenon was observed by other researchers under the same conditions; hydrogen bubbling through an aqueous solution, over a Pt/SiO₂ catalyst [5,6,24,30, 34]. The authors explained the effect by the instability of the metal particles (weaker metal-support interaction), due to a Me-H_{ads} binding energy that prevails over the metal-SiO₂ interaction. This allows for the migration of the unstable metal particles across the support causing agglomerating.

The use of DF imaging clearly shows advantages over BF when trying to identify particles. Whilst metal particles are seen using BF, there are areas of indiscernible

contrast. DF imaging resolves this problem clearly showing metal particles and even Sinfelts “metallic clusters”.



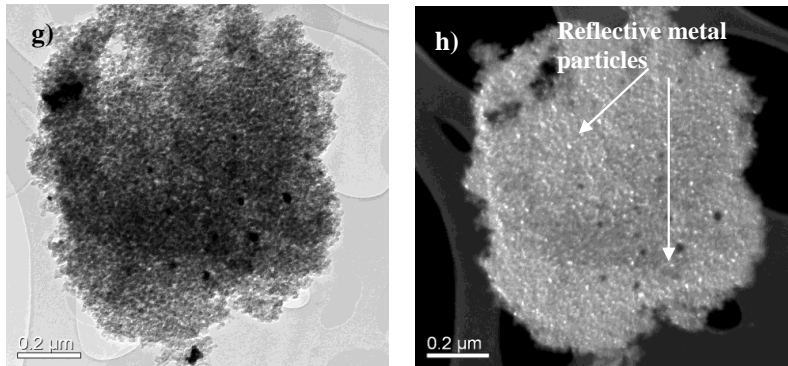


Figure 6: TEM images of 1.16%Pt-0.41%Ni/SiO₂ (Co-i) a) (BF), b) (DF); 1.57%Pt-0.72%Ni/SiO₂ (S-i) c) (BF) d) (DF); 0.83%Ni-1.37%Pt/SiO₂ (S-i) e) (BF) f) (DF) and 1.56%Pt-0.95%Ni/SiO₂ (Srr) g) (BF), h) (DF).

Figure 7 b) and c) show high magnification images of a metal cluster typically found on the 1.56%Pt-0.95%Ni/SiO₂ (Srr) catalyst. Particles were observed as small isolated crystallites or as aggregates on the support. This suggests that while migration of the particles does occur (lowering the dispersion) the particles maintain their individual small size. They don't fully agglomerate to form single large particles. A possible explanation for this may be that the Pt in a reduced state provides an electrostatic stabilization against full particle agglomeration and since there is not a recalcination step the particles are not miscible.

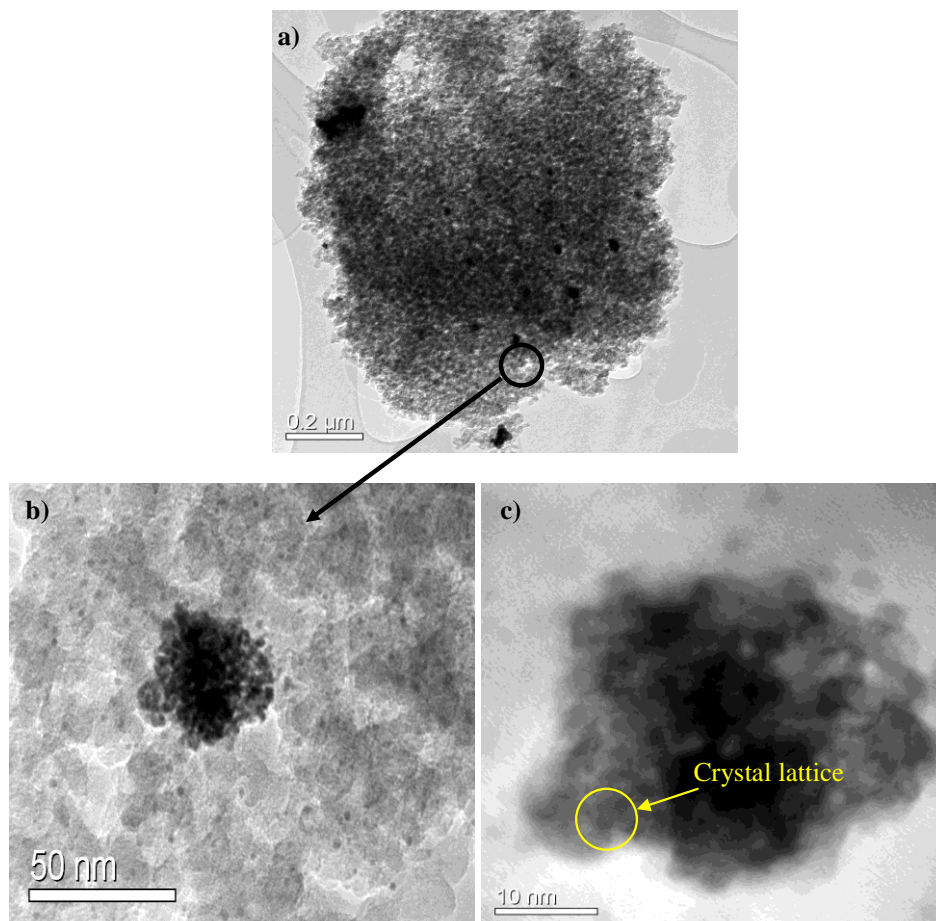


Figure 7: TEM images of 1.56%Pt-0.95%Ni/SiO₂ (Srr); a) bright field image, b) close-up magnification of surrounded area, and c) showing crystal lattice configuration

Scanning transmission electron microscopy (STEM), implemented on a conventional transmission electron microscope with STEM-attachment was used to analyze the bimetallic catalysts. STEM-EDX microanalysis (138 eV resolution) on a metal particle-by-particle basis, showed (on all four bimetallic catalysts) the simultaneous presence of Ni and Pt in some of the particles indicating the presence of bimetallic particles. Figure 8 presents the EDX analysis of metal particles on the 1.57%Pt-0.72%Ni/SiO₂ (S-i) catalyst. Metal composition in the particles ranged from Ni-rich to Pt-rich. This supports what was

seen in XRD diffraction patterns, the presence of the $\text{Ni}_{0.25}\text{O}_4\text{Pt}_3(210)$ bimetallic peak. Pt-only and Ni-only particles were detected in the Co-impregnated and successive impregnated catalysts, again corresponding with what was seen from XRD.

Predominantly, the Ni-only particles were found to be larger (averaging 32 nm) than the Pt-only particles (7-12 nm). The bimetallic particles identified were found in clusters and usually fell within the 15-25 nm range.

The 1.56%Pt-0.95%Ni/SiO₂ (Srr) catalyst did not show any individual metal particles, all particles examined showed a bimetallic composition, indicating that Pt and Ni were deposited into close contact and little or no monometallic particles were present on the support. Consistent particle sizes of 15-25nm were determined, with no large Ni particles or smaller Pt particles evident.

Comment [G1]: This is at odds with table 2 (7nm) and with the TEM images which show very small particles. Is this correct?

Wright *et al.* [23] reported no significant advantage in adding nickel to palladium catalysts for the hydrogenation of oil. They observed little differences in *trans* selectivity over various catalysts. The only benefit detected was an increase in catalytic activity, which occurred due to poison adsorption by the Ni. On the other hand, the results presented in Figure 3 indicate very obvious difference in selectivity towards C_{18:1} *trans*. A noticeable drop in activity was also evident following the addition of Ni to the Pt catalysts by co and successive impregnation. The activity was much less affected when Ni was deposited by surface redox reaction.

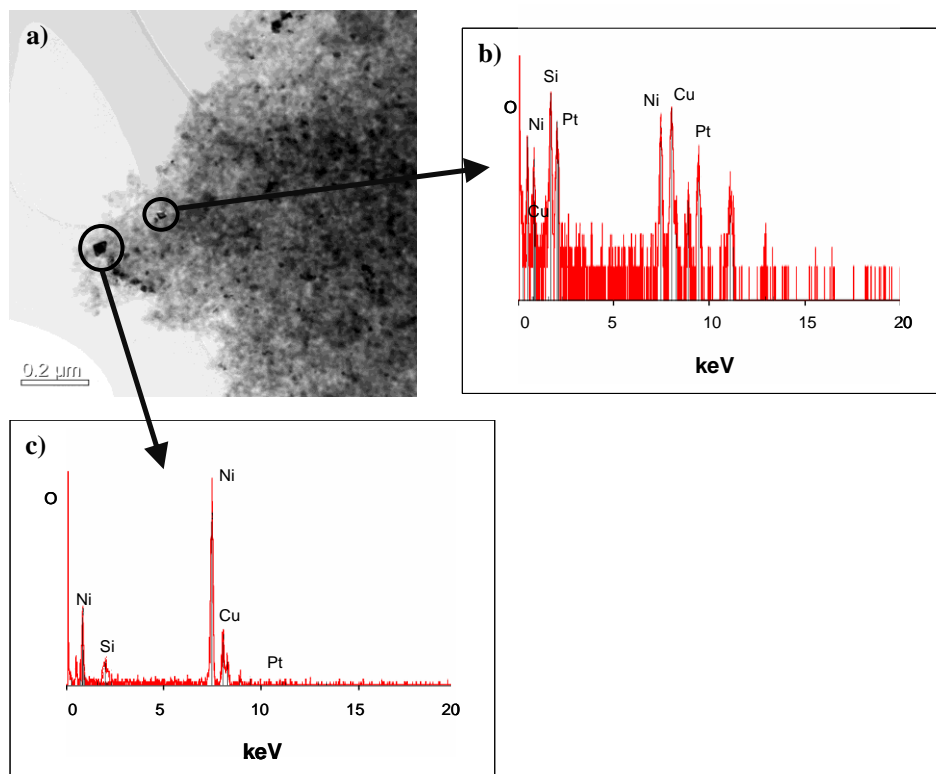


Figure 8: (a) TEM (bright field) of 1.57%Pt-0.72%Ni/SiO₂ (S-i); EDX analyze on metal particles on this catalyst shows the presence of a (b) bimetallic particle and (c) a Ni-only particle

In general, the behavior of the bimetallic catalysts resembled that of the monometallic Pt/SiO₂ catalyst, rather than the less active Ni catalyst. Results have shown that the surfaces of these bimetallic catalysts were composed of both Pt and Ni atoms as bimetallic entities and as individual monometallic particles. While it is known that the surface composition of alloys differ from the bulk, surface enrichment in the presence of adsorbed gas molecules has been documented for bulk alloys and bimetallic systems. Sedláček *et al.* [35] reported that the surface of the Pt-Ni alloys became enriched in Pt when the alloy was submitted to thermal treatments in H₂, hence the resemblance of the bimetallic systems to the Pt monometallic catalyst.

It has been reported that classical impregnation techniques like, co-impregnation and successive impregnation often prove to be unsatisfactory for bimetallic catalysts preparation. The main problem associated with these techniques is the failure to create an intimate contact between the two metals to obtain bimetallic entities. Lafaye et al. reported that the high temperature decomposition of the precursor salts in oxidative or reductive atmospheres does not lead necessarily to the formation of bimetallic species [24]. In order to optimize the interaction between the two metals the surface redox reaction (Srr) technique was employed.

It has been widely reported that the addition of Ni to Pt decreases markedly the adsorption strength of H₂ and hydrocarbons on the catalyst surface for a number of different reactions, including the hydrogenation of acetonitrile, ethylene hydrogenation and the study of the adsorption of H₂ and benzene [12, 18, 35-40]. This consequence may be considered in terms of two effects, one being an electronic interaction and the other an ensemble effect between the Ni and Pt. The electronic effect would change the strength of bonding of H₂ while the ensemble would affect the number of active sites available for adsorption. The change in activity on the bimetallic surfaces probably arises due to the geometric effect of the less active Ni blocking the Pt active sites, thus preventing the adsorption of C_{18:2} molecules and their subsequent hydrogenation. Dilution of the Pt metal by the Ni is another ensemble effect observed. This ensemble or geometric effect probably counts for the change in activity and selectivity seen on the traditional synthesized catalysts, co and successive impregnated, due to the nature of the

deposition of the Ni onto the Pt. The existence of a subsurface Ni layer in a bimetallic Pt/Ni catalyst is acknowledged in the literature [35, 37, 39]. The presence of this sub-layer gives rise to particle effects such as twinning and dislocations. The geometric arrangement of the quasi-complete Pt overlayer has an effect on the reaction selectivity by changing the chemisorption properties of the reactants [17, 18, 41].

While such a geometric interpretation can account for the change in the conventional synthesized catalysts it does not explain the results obtained by the Srr catalyst. The catalytic activity of 1.56%Pt-0.95%Ni/SiO₂ (Srr) was only marginally reduced compared to the monometallic 1.57%Pt/SiO₂ catalyst, while the selectivity towards C_{18:1} *trans* was distinctly increased (formed ~10% less *trans* isomers). It is difficult here to dismiss the possibility that the electronic interaction between the Ni and Pt affected the hydrogenation reaction.

Bertolini [41] was the first to explain the influence of strain in the electronic properties of the surface atoms as the most probable reason for the modification of the chemical reactivity of Pt-Ni alloys. Boitiaux *et al.* [38] studied the effects of additives on adsorption coefficients. Co-adsorption, on the catalyst surface, of electron-attracting compounds is inclined to increase the adsorption strength of a hydrocarbon. As already noted the addition of Ni to Pt reduces the adsorption strength of H₂ and hydrocarbons, thus indicating an electron donor effect. Nohair [5, 6] reported that this electron donor effect would increase the electron density of the metal particles, and thus weaken the adsorption of the C_{18:1} molecules on the catalysts surface. Since hydrogenation is accompanied by an

isomerisation process, resulting from competing dehydrogenation of the intermediate chemisorbed radical [42] it can be proposed that the electron donor characteristic would also affect this reaction. If the chemisorbed intermediate is removed quickly enough it may not have time to isomerize to *trans*. This modification of the electronic properties and the presence of the geometric effect both may be used to explain the limited formation of C_{18:1} *trans* compared to that of the monometallic Pt catalyst.

4. Conclusions

From the results it is clear that the addition of Ni to the Pt/SiO₂ catalyst has a beneficial effect on the selectivity of the hydrogenation reaction. The 1.57%Pt/SiO₂ catalyst forms 26.5% *trans* at an IV of 70. Using the classic method of synthesizing bimetallic catalysts, co-impregnation, it can be seen that the addition of Ni lowers the *trans* content to 23% at a similar IV of 70. A further reduction was observed when the catalysts were prepared by surface redox reaction (Srr), whereby the selectivity fell to 16.8%. This change in selectivity seems to be related to the weakened adsorption of the C_{18:1} molecules on the catalysts surface. The method in which the bimetallic catalysts are prepared is also important for the overall activity. The classical preparation methods of co-impregnation and successive impregnation seem to have a negative effect on the activity of the reaction. With these impregnation methods the relatively inactive Ni may block the highly active Pt particles, thus resulting in a drop in activity. Using the Srr method prevents this 'blocking' effect.

4.0 References

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