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Platinum supported on nanosilica and fibrous nanosilica for hydrogenation reactions

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ABSTRACT

Platinum nanoparticles supported on nanosilica (NP) and fibrous nanosilica (dendritic fibrous nanospheres, DFNS) were prepared by direct grafting of the Pt precursor onto the silanol groups or via a polyethylenimine (PEI) linker. From the SEM and TEM images the average diameter of the nanosilica and fibrous nanosilica (DFNS), was determined to be 21.4 and 503 nm, respectively. While surface areas as measured by ASAP is 463.4 m² g⁻¹ for DFNS and 142.5 m² g⁻¹ for the nanosilica. For the four Pt containing catalysts (Pt/NP, Pt/DFNS, Pt/PEI/NP and Pt/PEI/DFNS), a Pt loading between 1.35×10^{17} and 8.46×10^{17} Pt atoms per gram support were determined. The PEI-containing catalyst gave higher Pt-loading than the direct anchoring of the Pt onto the silanol groups of the support. The catalysts were further characterised ATR FTIR and XPS. After oxidation of the pre-catalysts 85% of the Pt was in the oxide form. While after reduction, ca. 82% the Pt supported on DFNS was in the metallic form. Reduction of the Pt supported on NP, resulted in 100% of the Pt in the Pt⁰ oxidation state. These catalysts were tested for the hydrogenation of C=C and/or C=O bonds in cyclohexene, benzaldehyde and cinnamaldehyde. The % conversion and product distribution will be discussed in term of diameter, surface area and Pt-loading.

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1. Introduction

Metal-containing heterogeneous catalysts usually consist of transition metals deposited onto the surface of the solid support as the active phase of the catalyst [1]. When the catalytically active species are supported by metal oxides, the support may also offer additional catalytic functionality that may also improve the overall catalytic performance [2]. Upon choosing a suitable catalytic support, one has to consider the surface area, thermal, mechanical and chemical stability [1,3,4]. Silica has been used as a starting precursor due to its benign nature, low toxicity, ease of surface modifications, chemical and mechanical stability [5].

The oxide groups on silica are unreactive towards binding with metal precursors. The first important surface modification on silica supports is, therefore, the hydroxylation of the silicon oxide, which affords reactive silanol groups (Si-OH) [6]. The silanol groups can then be used for direct binding of the metal precursor or to bind other entities with different functional groups, which can act as anchoring sites. These include alkoxysilanes [4,7–10], and dendrimers [1,11,12],which have been used as a way of controlling

the amount of metal ions deposited onto the support, the particle size and metal distribution [13,14].

The fundamental properties that describe the efficiency of a heterogeneous catalyst are: activity, selectivity, reproducibility, affordability, thermal and mechanical stability. This also include morphological characteristics like high surface area, high number of active sites per unit area and crystallinity [15]. Consequently, it is important to maximize the surface area and the number of the active sites to improve the catalytic performance.

Porous material (known to have a large surface area) have been used for various applications, such as biological and pharmaceutical systems [16–18], gas storage and chemical sensing [19]. One of the major uses of porous materials is in heterogeneous catalysis [20]. The pores increase the surface area dramatically, which allows for anchoring of more catalytically active sites (metals) [21], than a smooth surface with the same volume. Pores are not the only way to increase the surface area, fibrous extensions protruding from the core of a particle can also increase surface area. In 2010, Polshettiwar et al. [22,23] discovered fibrous silica or dendritic fibrous nano-spheres (DFNS). Fibrous silica has high surface area owing to its fibrous morphology, ranging from 500 to 600 m² per g [24,25]. This material also exhibits physical properties such as good thermal, hydrothermal and mechanical stability [4].





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Fibrous silica (DFNS) has also been used as a solid support in heterogeneous catalysis. The fibrous morphology of DFNS not only increases the surface area of the silica particle but also the accessibility of active metals during catalysis, making it a very useful support [1,22]. Fibrous silica have a wide variety of applications such as CO_2 adsorbent, catalytic support as well as solar energy harvest [26,27]. Because fibrous silica is nontoxic and biocompatible, it has found applications as a component for efficient drug delivery.²⁶

To improve the stability of supported catalysts, research has also focussed on the use of polyethylenimine (PEI) as an alternative to organofunctional silane to modify the support surface [18,25,28,29]. PEI is a polycationic molecule with repeating units of primary, secondary and tertiary amino groups separated by a CH₂-CH₂ spacer [30,31]. The amino groups on PEI are active and form strong metal-N ligand complexes and hydrogen bonds with surface silanols [32,33]. PEI is often used as a pseudoligand, which helps in homogeneously dispersing metal nanoparticles and maintains their stability against leaching [18,34].

Platinum is one of the most commonly used metals in chemical catalytic reactions such as hydrogenation and dehydrogenation [35]. It can easily donate or accept electrons. This result in changes in the oxidation states (Pt^0 , Pt^{II} and Pt^{IV}) during the catalytic cycle [36–38]. The catalytic performance of platinum is enhanced when it is present as nanosized particles that are homogeneously distributed on the solid support [39,40].

The hydrogenation of unsaturated aldehydes to saturated alcohols was first introduced a century ago and has been an important industrial process ever since [41]. This type of a reaction can produce three products: unsaturated alcohols due to the reduction of the C=O bond, saturated aldehydes due to the reduction of the C=C bond and saturated alcohols due to the complete reduction of both functionalities [42]. Unsaturated alcohols are important intermediates for the production of fine chemicals, perfumes and pharmaceuticals and as such, have attracted a lot of attention around them [41,43,44].

The purpose behind this study is to compare nanosilica powder and DFNS as catalytic supports for platinum. The effect that the hydroxylated- and polyethylenimine (PEI)-modification have on surface area, Pt-loading and catalytic activity towards hydrogenation will be investigated. Each modification will be characterised by different surface, elemental and structural characterisation methods. A brief analysis on the catalytic activity, product distribution of the catalyst will also be conducted.

2. Experimental

2.1. Materials and spectroscopic characterisation

Liquid and solid reagents were purchased from Sigma Aldrich and Merck Chemicals and were used without further purification. X-ray photoelectron Spectroscopic (XPS) measurements was conducted on a PHI 5000 Versaprobe system, equipped with a monochromatic Al K α X-ray source (Al K α = 1486.6 eV). Operating conditions and settings are similar as reported in previous work from this lab [45–49]. SEM images was captured using a Shimadzu Superscan ZU SXX-550 electron microscope. TEM was performed with a Phillips (FEI) CM100 equipped with a Megaview III digital camera and coupled to an Oxford X-Max (80 nm²), energy-dispersive X-ray spectroscope (EDS). ATR-FTIR spectra were recorded from neat samples on a Digilab FTS 2000 Fourier transform spectrometer utilizing a He-Ne laser at 632.6 nm. TGA experiments were performed on a TGA/SDTA851e instrument. All porosity and surface area properties were determined on a Micromeritics ASAP 2020.

2.2. Catalyst preparation

2.2.1. Synthesis of fibrous nanosilica (DFNS) [50]

A mixture of urea (1.213 g, 0.020 mol), water (60 ml) and cetyltrimethylammonium bromide, CTAB, (2.006 g, 0.00550 mol) was stirred for 15 min. Tetraethyl orthosilicate, TEOS) (5.00 g, 0.024 mol) was dissolved in cyclohexane (60 ml) and this was added dropwise in the urea mixture solution. The mixture was stirred for a further 15 min and then 1-pentanol (3 ml) was added dropwise. The resultant solution was stirred for 30 min at ambient temperature, transferred to a Teflon-lined autoclave reactor and heated for 5 h at 120 °C. The suspension was cooled to room temperature and the product was recovered by centrifugation, washed with water and acetone and dried in air for 24 h followed by calcination at 550 °C for 6 h [50].

IR ν [cm⁻¹]: 807 (Si-O-Si) symmetric stretch, 1040 (Si-O-Si) asymmetric stretch, 3500 (Si-OH),

2.2.2. Functionalisation of silica supports with branched polyethylenimine

The silica supports, either nanosilica or DFNS (5.0 g) was degassed in vacuo at 120 °C for 12 h and then cooled to 60 °C under Argon. (3-Glycidyloxypropyl)trimethoxysilane, GTMS, (5.2 ml) dissolved in hot methanol (30 ml) was added to the degassed silica supports with continuous stirring for 1.5 h. Branched polyethylenimine (PEI) (5.00 g) was dissolved in hot methanol (30 ml) and then added to the reaction mixture. The resultant solution was stirred for 5 h at 60 °C. The functionalised supports was recovered by centrifugation, washed with hot methanol three times and then dried in vacuo for 12 h.

DFNS: IR v [cm⁻¹]: 807 (Si-O-Si) symmetric stretch, 1040 (Si-O-Si) asymmetric stretch, 1500 (C–N), 1650 (1° N–H), 2800–2950 (C–H), 3600–3000 (Si-OH, 1° and 2° N–H).

Nanosilica: IR ν [cm⁻¹]: 807 (Si-O-Si) symmetric stretch, 1040 (Si-O-Si) asymmetric stretch, 1500–1650 (C–N), 1650 (1° N–H), 2800–2950 (C–H), 3600–3000 (Si-OH, 1° and 2° N–H).

2.2.3. Grafting of $PtCl_2$ onto the silica supports

The as prepared DFNS or nanosilica (100 mg) was added to a solution of $PtCl_2$ (10 mM, 5 ml) in chloroform. The suspension was stirred at room temperature for 24 h. The platinated surfaces were recovered by centrifugation followed by continuous washing with CHCl₃ to remove the unbound $PtCl_2$ and dried in a nitrogen stream.

2.2.4. Calcination and reduction of the Pt-grafted silica supports

The silica supports grafted with Pt were calcined in a reduction oven in air by increasing the temperature with 5 °C per minute to 250 °C and the same temperature was maintained for 3 h. This was followed by subsequent cooling to room temperature. For the reduction step, the calcined sample were heated in a reduction oven under flowing H₂ by increased the temperature with 5 °C per minute to 350 °C and the same temperature was maintained for 3 h. The samples were stored in a glove box.

2.3. Catalytic test reactions

2.3.1. Hydrogenation of 1-cyclohexene

The silica supported Pt catalysts were activated before the catalysis was commenced.¹ 1-Cyclohexene (1 ml) dissolved in *n*-hexane (3 ml) were added to the activated catalyst in the reactor followed by flushing of H_2 three times. The reactor was sealed under

 $^{^1}$ The silica supported Pt catalysts (10 mg) was loaded in a Parr Reactor. The catalyst was activated by flushing the reactor containing the catalyst with H₂ three times. The Pt was reduced at 150 $^{\rm e}$ C and 15 bar H₂ pressure overnight.

 H_2 at 15 bar. The reaction was carried at 60 °C for 6 h which stirring at 250 rpm. The crude reaction mixture was analysed by ¹H NMR.

2.3.2. Hydrogenation benzaldehyde

Benzaldehyde (1 ml) dissolved in *n*-hexane (3 ml) were added to the activated Pt catalyst^{*} in the reactor followed by flushing of H₂ three times. The reactor was sealed under H₂ at 15 bar. The reaction was carried at 60 °C for 6 h which stirring at 250 rpm. The crude reaction mixture was analysed by ¹H NMR.

2.3.3. Hydrogenation cinnamaldehyde

Cinnamaldehyde (1 ml) dissolved in *n*-hexane (3 ml) were added to the activated Pt catalyst^{*} in the reactor followed by flushing of H₂ three times. The reactor was sealed under H₂ at 15 bar. The reaction was carried at 60 °C for 6 h which stirring at 250 rpm. The crude reaction mixture was analysed by ¹H NMR.

3. Results and discussion

Fibrous silica was prepared according to the adapted method of Dong et al. [54] The preparation of fibrous nanosilica (DFNS) involves the formation of microemulsions. Cetyltrimethylammonium (CTAB) is used as a surfactant, which directs the structure of the silicate molecules (TEOS is used as a silica precursor) and is eventually removed during calcination [51], while the urea is used as the hydrolysing agent [52]. The transmission electron microscope (TEM) and scanning electron microscope (SEM) images of the as-prepared DFNS, Fig. 1, shows well-defined and ordered fibres, which are evenly distributed around the particle. The average particle size is 503 nm and from the TEM image it appears that the fibres cover the outer ca. 120 nm of the particles. The particle size distribution curves and statistical data obtained from the TEM images are also shown in Fig. 1.

For comparison with the purchased nanosilica, the TEM images along with the particle size distribution curves and statistical data are presented in Fig. 2. The mean particle size of the nanosilica is ca. 21.4 nm. The nanosilica is one order of magnitude smaller than the DFNS.

The BET surface area and pore volume was determined using accelerated surface area and porosity analyses (ASAP) with N_2 at





77 K, see Table 1 for the data. The N₂ isotherms for the DFNS and nanosilica surfaces are shown in the Supplementary information. DFNS gave the highest surface area, $463.4 \pm 3.24 \text{ m}^2 \text{ g}^{-1}$, while the nanosilica had a surface area of $142.50 \pm 1.28 \text{ m}^2 \text{ g}^{-1}$.

From the substantial difference in size and surface area, we will be able to investigated the influence of the smaller size of the nanosilica and the increased surface area of the DFNS on Pt-loading and eventually catalysis.

The silica supports are functionalised with Pt, using different two methods (see Scheme 1). Direct grafting of PtCl₂ on the silanol groups of the supports (to produce Pt-O bonds), this resulted in the Pt-supported nanosilica, Pt/NP, and the Pt-supported fibrous silica, Pt/DFNS. The second route involves the immobilisation of PtCl₂ onto the surfaces functionalised with polyethylenimnine (PEI) linkers (this produces Pt-N bonds). This resulted in the Pt-supported via PEI nanosilica, Pt/PEI/NP, and the Pt-supported via PEI fibrous silica, Pt/PEI/DFNS.

The PEI functionalised supports was prepared by first attaching the (3-glycidyloxypropyl) trimethoxysilane (GTMS) onto the silanol groups. The branched polyethylenimine (PEI) was anchored via an epoxy-amine cross-linking reaction of the epoxide group on the GTMS and an amine group on the PEI.

The functionalisation of the silica supports with PEI, decreased the surface area. PEI-functionalised DFNS has a surface area of 70.34 \pm 0.57 m² g⁻¹, (an 85% decrease in surface area compared to unmodified DFNS. While the PEI-functionalised nanosilica has a surface area of 126.91 \pm 0.00 m² g⁻¹, an 11% decrease in surface area as compared to the unmodified nanosilica. After PEI-modification the nanosilica has a larger surface area than the DFNS. The BET surface area and pore volume of all four of the Pt-functionalised silica supports and their precursors are summarised in Table 1. The N₂ isotherms for PEI- and Pt-functionalised supports are shown in the Supplementary information. From the comparison of the SEM images of the DFNS before (Fig. 1) and after PEI-functionalisation, it looks like the PEI pseudo-ligand closes the pores (which dramatically deceased the surface area), however, the structure remains intact.

Since the chemisorption technique measures only the exposed metal not the bulk, the amount of exposed Pt atoms per g of catalysts could be determined and as a consequence per 10 mg, which is the amount used during the catalytic reactions (this will be used to determine the product formation frequency, PFF). The atomic radius of Pt⁰ is 1.77×10^{-10} m, thus the surface area of a Pt atom is 9.84×10^{-20} m² (as calculated with a = π r²). The metallic area of the sample (of the catalyst, Pt on the support) was determined from ASAP, dividing this metallic area with surface area of one Pt atom, the amount of Pt atoms per gram of sample (the catalyst) could be determined. As an example, the calculations for Pt/DFNS will be shown below.

amountofPtatomspergramofcatalyst

$$= \frac{\text{Metallicareaofsample}(m^2g^{-1})}{\text{surfaceareaofonePtatom}(m^2)}$$

amountofPtatomspergramofcatalyst
$$= \frac{0.0133m^2g^{-1}}{9.84x10^{17}m^2}$$
$$= 1.35x10^{17}g^{-1}$$

 $amount of Ptatom sper 10 mg of catalyst = 1.35 x 10^{17} g^{-1} x 0.01$

$$= 1.35 \times 10^{15} (10 mg)^{-1}$$

The amount of Pt-atoms per m^2 , was determined by dividing the amount of Pt-atoms per g by the BET surface area (measured in $m^2 g^{-1}$). Even though the nanosilica has a smaller surface area than DFNS, more Pt atoms was loaded onto it per m^2 . After



Fig. 2. The TEM (Left) of the purchase nanosilica, the particle diameter (ø), and the histogram.

Table 1

BET surface area, micropore volume and dispersion values obtained from accelerated surface area and porosity analyses (ASAP) with N₂ at 77 K. As well as the surface area data obtained from chemisorption of CO at 35 °C, the % dispersion, metallic area of the sample, metallic area of the metal, Pt atoms per g, Pt atom per 10 mg (the amount of catalyst used), mol Pt per 10 mg of catalyst and amount of Pt atoms per m².

Sample	Physisoption data			Chemisorption da	Pt atoms /				
	BET Surface Area (m ² .g ⁻¹)	<i>t</i> -plot Micropore Volume (cm ³ .g ⁻¹)	Dispersion (%)	Metallic area of sample (m ² /g)	Metallic area of metal (m²/g)	Pt atoms /g	Pt atoms / 10 mg	mol Pt / 10 mg	m²
DFNS	463.4 ± 3.24	0.086							
Pt/DFNS	134.15 ± 0.85	0.0002	0.1535	0.0133	0.3790	1.35×10^{17}	1.35×10^{15}	2.24×10^{-9}	2.91×10^{14}
PEI/DFNS	70.34 ± 0.57	0.006							
Pt/PEI/DFNS	92.04 ± 0.71	0.023	0.2883	0.0335	0.7119	3.40×10^{17}	3.40×10^{15}	5.65×10^{-9}	4.83×10^{15}
NP	142.50 ± 1.28	0.013							
Pt/NP	146.63 ± 1.55	0.018	0.2250	0.0630	0.6297	6.40×10^{17}	6.40×10^{15}	1.06×10^{-9}	4.49×10^{15}
PEI/NP	126.91 ± 0.00	0.025							
Pt/PEI/NP	99.27 ± 0.86	0.065	0.3371	0.0832	0.8324	$\textbf{8.46}\times 10^{17}$	$\textbf{8.46}\times 10^{15}$	1.40×10^{-9}	6.67×10^{15}

PEI-functionalisation, the PEI/DFNS showed a ca. 16 times increase in Pt loading per m^2 , while PEI/NP Pt loading per m^2 increased ca. 1.5 times. This clearly indicates that the functionalisation with the PEI increases Pt loading per m^2 .

To further confirm the success of the covalent attachment of PEI, ATR FTIR analysis was conducted. The ATR FTIR spectra of the as-prepared DFNS, the nanosilica as well as the PEI-modified supports are shown in Fig. 3. The absorption bands of the asymmetric stretch and distortion forms of the siloxane (-O-Si-O-) groups are in the range 1040–1050 cm⁻¹, while, the band at 807 cm⁻¹ is assigned to the symmetric stretch of -O-Si-O-[53]. The broad absorption band at the 3000–3600 cm⁻¹ region is characteristic of the OH peak from the Si-OH atoms and the H-O-H anti-symmetric and symmetric stretching frequencies from the water molecules adsorbed on silica. From the ATR FTIR of DFNS and nanosilica, it is evident that silanol groups are already present on the surface, most probably formed during preparation.

The appearance of additional bands upon GTMS and PEI functionalisation of the silica supports is indicated in the blocks in the ATR FTIR spectra (Fig. 3). The C—H vibrations due to the presence of the GTMS and PEI were observed in the range 2800– 2950 cm⁻¹. The absorption bands at 1500 and 1650 cm⁻¹ are assigned to C—N stretching vibrations and bent N—H asymmetric stretching from the 1° amines [54,55].

The modified silica supports were characterised by X-ray photoelectron spectroscopy (XPS). XPS is a surface sensitive technique that is used to determine the elemental composition and chemical states of the elements present on solid materials. The analysis involves the measurement of the kinetic energy of the photoelectrons emitted from the sample surface and translates it to the binding energy of the photoelectrons [56–58]. These binding energies are unique for each element and also depend on the oxidation state and chemical environment of the element. One can then deduce the elements present on the surface and their oxidation state based on the corresponding binding energy value. Adventitious oxygen and carbon are always present on all samples. This adventitious carbon is used to correct for any charging effects observed in all the other measured peaks of importance. The lowest binding energy of the fitted adventitious C 1 s peak was set at 284.8 eV. The Si 2p photoelectron envelope showed a maximum counts per seconds at ca. 102.4 eV for all four catalysts. The PEI-containing catalyst showed the additional N 1 s photoelectron line at ca. 398.5 eV. The N 1 s photoelectron envelope could be simulated with three peaks representing the 1° , 2° and 3° amines at ca. 397.6, 398.9 and 400.7 eV, respectively. The XPS spectra of the C 1 s, Si 2p and N 1 s photoelectron lines from PEI/DFNS is shown in the supplementary information as an example.

XPS was also used to analyse the Pt-modified supports. Fig. 4 shows high resolution XPS spectra of the Pt 4f photoelectron lines and tabulated binding energies of the as prepared Pt/DFNS as well as in the oxidized and reduced state.

The XPS spectra of the Pt 4f photoelectron envelopes shows well defined peaks with a spin-orbit-splitting of ca. 3.3 eV between the Pt $4f_{7/2}$ and Pt $4f_{5/2}$. Depending on the sample and treatment, these photoelectron envelopes were fitted with either one, two or three sets of Gaussian peaks. The Pt 4f 7/2 photoelectron lines of the PtCl2 is present at ca. 73.6 eV, the PtO at ca. 72.3 eV and the Pt⁰ at ca. 71.0 eV, all in correlation with published values [59–61]. For all the samples, oxidation only leads to the formation of ca. 85% PtO, while the reduction seemed to be support dependent. Only ca 82% of the Pt on the DFNS and PEI/DFNS reduced to Pt⁰, while the nanosilica gave 100% reduction of the Pt on both umodified and PEI-modified nanosilica. The 100% reduction of the Pt on the nanosilica is probably due to better exposure of the Pt to the H₂ atmosphere, since it does have a large micropore volume. For the DFNS, some of the Pt-moieties are "hidden" in the fibres, also explaining the presence of some PtCl₂ after oxidation and reduction.

The Pt-supported catalysts were tested for the hydrogenation of C=C and/or C=O bonds in cyclohexene, benzyl alcohol and



Scheme 1. The anchoring of PtCl₂ directly on the silanol groups of the supports (route A) or via polyethylenimnine (PEI) linkers on the silica supports (route B).

cinnamaldehyde. This was done to investigated the influence of the different solid supports (the size and surface area) as well as the influence of the PEI addition onto the support on the hydrogenation of double bonds.

Cyclohexene (3 M in *n*-hexane) was hydrogenated over the in situ reduced Pt-supported catalysts (it is assumed that all Pt is now in the metallic state) at 60 °C and 15 bar H₂ pressure. After 6 h, the crude reaction mixture was subject to ¹H NMR spectroscopy. The disappearance of the signals at 5.70, 2.0 and 1.63 ppm representing the protons cyclohexene as well as the appearance of the singlet at 1.5 ppm representing the cyclohexane, confirmed the 100% conversion of cyclohexene to cyclohexane (see supporting information for the ¹H NMR spectra).

Benzaldehyde (3 M in *n*-hexane) was hydrogenated over the in situ reduced Pt-supported catalysts at 60 °C and 15 bar H_2 pressure. The possible hydrogenation products that could form is benzyl alcohol (form by hydrogenation of the carbonyl group), toluene (formed by the follow-up hydrogenation of the –OH of the benzyl alcohol) and the over reduced product methylcyclohexane.

The analysis of the ¹H NMR of the crude reaction mixtures collected after 6 h showed the characteristic methylene protons of the benzyl alcohol at 4.7 ppm and methyl protons of toluene at 2.2 ppm (see Supplementary Information). The characteristic methyl protons of methylcyclohexane at 0.9 ppm was absent, indicating that over reduction did not occur.

However, a doublet at 8.12 ppm appears in the ¹H NMR spectra of the crude reaction mixture catalysed by the Pt/PEI/NP, Pt/DFNS and Pt/PEI/DFNS. This doublet is assigned to the two –CH- protons ortho to the carboxylic acid group of benzoic acid (confirmed by comparison of with an ¹H NMR spectra of pure benzoic acid) [62]. The presence of the benzoic acid is unexpected in a hydrogenation reaction. This imply that during the hydrogenation some trace amounts of water present (probably present in the reagent or due to complete hydrogenation of the –OH groups on the alcohols) oxidised the benzaldehyde via the classical hydration to form a germinal diol preceding the dehydrogenation to benzoic acid as illustrated in Scheme 2 [63]. The characteristic singlet at 6.1 ppm



Fig. 3. ATR FTIR spectra from the top to the bottom, of the GTMS and PEI-modified nanosilica (PEI/NP), nanosilica (NP), the PEI-modified fibrous silica (PEI/DFNS), and fibrous silica (DFNS).

of the methylene proton of the diol intermediate was not detected in ¹H NMR. The % conversion of benzaldehyde and % selectivity towards benzyl alcohol, toluene and benzoic acid for each catalyst is given in Table 2 as well as the product formation frequency, PFF, (in s^{-1}). PFF is calculated using the following equation:

	/amountofmoleculesofproductformed					
PFF =	amountofPtatoms					
	time(s)					

The calculation of the PFF for benzyl alcohol over Pt/PEI/NP will be discussed as an example. The total amount of benzaldehyde molecules is 8.42×10^{21} (1 ml benzaldehyde = 1.04 g = 9.8×10^{-3} mol = 8.42×10^{21} atoms). Multiplying this value with the % converted to benzyl alcohol, which is 21.3% (38% total conversion \times 56% selectivity towards benzyl alcohol = 21.3%) gives 2.72×10^{21} molecules which was converted to form benzyl alcohol. From the chemisorption data in Table 1 (where the amount of Pt atoms per 10 mg was determined), the amount of Pt atom present in Pt/PEI/NP was 6.40×10^{15} . Inserting these values in the above equation, where time is 21 600 s (6 h) the PFF could be calculated.

Pt/PEI/DFNS gave the highest total conversion, best selectivity and PFF towards benzyl alcohol. The second catalytic cycle using Pt/PEI/DFNS gave only a 6.5% conversion to benzyl alcohol. This is one order of magnitude smaller than the fresh catalyst, indicating poor recyclability. The used catalyst (after the first catalytic cycle) was characterised by SEM and XPS (see Supplementary Information). Visually the structure of the DFNS remains intact, but the fibres seem to be more separated from each other. While the XPS of the used catalysts showed that all Pt present was in the metallic form. This is expected to increase the catalytic activity, which was not the case. However, from the ratios (obtained from the XPS) of Si:N:Pt of Pt/PEI/DFNS before (1:1.4:0.88) and after (1:0.2:0.2) catalysis, it is clear that there was a dramatic decrease



Fig. 4. XPS data of Pt 4f photoelectron lines for the as-prepared Pt/DFNS, as well as after calcination and reduction.



Scheme 2. Schematic representation of the benzaldehyde dehydration to benzoic acid.

in N- and Pt-content after catalysis. This could possible explain the decrease in catalytic activity.

Pt/DFNS gave the second highest conversion, however considering that it was 88.6% selective towards the formation of benzoic acid, which is an uncatalysed hydration/dehydrogenation sidereaction, the total catalysed conversion is only 4.4%.

The general trend seems to be the higher that amount of Pt atoms present on the support, the higher the catalysed conversion (not considering the formation of benzoic acid). The exception to this rule is Pt/PEI/DFNS, which gave much higher conversion. The bar graphs showing the % selectivity and PFF is given in the supplementary information.

Cinnamaldehyde has two double bonds (C=C and C=O), which are susceptible and in competition for hydrogenation. The hydrogenation of cinnamaldehyde can proceed via three different pathways as shown in Scheme 3. The hydrogenation of the carbonyl group (C=O) to form cinnamyl alcohol, an unsaturated alcohol (pathway 1). The hydrogenation of the carbon–carbon double bond to form phenyl propionaldehyde, a saturated aldehyde (pathway 2), or the complete hydrogenation of both functional groups to form 3-phenyl propanol (pathway 3).

The selectivity for the hydrogenation of cinnamaldehyde has been reported as challenging in literature [64–66]. because of the different intermediates and by products that may form. The hydrogenation of the C=C bond is thermodynamically favoured by about 35 kJ/mol over the hydrogenation of C=O [67], which makes the selectivity of this reaction even more difficult to achieve.

A 2.6 M cinnamaldehyde in isopropanol was hydrogenated for 6 h in a pressurised vessel at 15 bar H_2 and 150 °C, over prereduced Pt/NP, Pt/DFNS, Pt/PEI/NP and Pt/PEI/DFNS. ¹H NMR analysis was used to determine the % conversion and product distribution of the crude reaction mixture. See the supplementary information for the ¹H NMR spectra and Table 3 for the data.

The characteristic ¹H NMR signals used to determine the product distribution is: the singlet aldehyde signal at 9.8 ppm of 3-phenyl propionaldehyde, doublet signal of the aldehyde of cinnamaldehyde at 9.7 ppm, two sets of the doublet signals centred at 7.8 and 6.49 ppm representing the olefinic methine protons of cinnamic acid, a set of doublets centred at 4.3 ppm assigned to the methylene protons α to the –OH group of cinnamyl alcohol, and lastly a triplet centred around 3.7 ppm representing the methylene protons α to the –OH group of 3-phenyl propanol.

The presence of cinnamic acid in the crude reaction mixture implies that during catalytic hydrogenation, cinnamaldehyde is oxidised. This oxidation occurs probably via the classical hydration to the germinal diol followed by dehydrogenation to cinnamic acid





Scheme 3. Reaction scheme for the hydrogenation of cinnamaldehyde.

similar to the formation of the benzyl alcohol (the scheme is given in the supplementary information) [68,69]. The intermediated diol was not detected in the NMR spectra.

The bar graphs in Fig. 5 indicates the % selectivity and PFF (s^{-1}) toward the different products of the hydrogenation of cinnamaldehyde over each of the catalyst. With the exception of Pt/DFNS, which favour the formation of 3-phenyl propanol, the selectivity towards cinnamyl alcohol (the most desired product) is favoured by all the catalysts. Pt/DFNS showed the highest PFF for both 3-phenyl propanol and cinnamyl alcohol.

The success of a catalyst is measured by its % selectivity and/or the PFF towards the desired product. For the hydrogenation of benzaldehyde and cinnamaldehyde, the desired products are benzyl alcohol and cinnamyl alcohol, respectively. The factors that can influence the % selectivity and/or the PFF towards the desired product is: the total BET surface area in m² g⁻¹ of the support (**A**), diameter of the support (**D**) and/or the Pt surface area in m² g⁻¹ (**P**). Each individual factor's influence on % selectivity and/or the PFF towards the desired product as well as different combinations of the factor's influence on % selectivity and/or the PFF towards the desired product was compared (see supplementary information). A significant influence is measured by how good a linear relationship could be fitted to the data, a R² value > 0.8 is considered significant.

From this the data compared it can be concluded that the individual or combination of factor's (A, D and P) has no significant influence on the % selectivity towards the desired products.

The PFF for benzyl alcohol is influenced by the combination of the **D** × **P** as well as the combination of **A** × **D** × **P**. The combination of the selectivity and PFF towards benzyl alcohol is influenced by the combinations of **D** × **P** as well as **A** × **D** × **P**.

The PFF of the formation of cinnamyl alcohol is dependent on **D**, as well as the combination of the $\mathbf{A} \times \mathbf{D}$ as well as $\mathbf{A} \times \mathbf{P}$. The combination of PFF and % selectivity towards the cinnamyl alcohol is dependent **D**, as well as the combination of the $\mathbf{A} \times \mathbf{D} \times \mathbf{P}$.

From this it can be concluded that obtain high selectivity towards the desired product as well as a good PFF, all the factors that can influence the activity is important to consider, no single factor is more important than the others. Thus a high surface area of the support, a small diameter of the support and high Pt-loading.

Table 2

The % conversion and % selectivity towards benzyl alcohol and toluene per catalyst of the hydrogenation of benzaldehyde as well as the product formation frequencies (PFF) in s^{-1.}

Catalyst	% Conversion	% Selectivity						
		benzyl alcohol	$PFF(s^{-1})$	toluene	$PFF(s^{-1})$	benzoic acid	$PFF(s^{-1})$	
Pt/NP	12.4	76.7	5.78	23.3	1.77	>0.1	-	
Pt/PEI/NP	38.0	56.0	9.82	>0.1	-	44.0	7.69	
Pt/DFNS	38.5	6.5	7.22	4.9	5.49	88.6	98.46	
Pt/PEI/DFNS	62.9	73.4	52.97	1.4	1.03	20.2	18.11	
Used Pt/PEI/DFNS	6.5	100	149.05	-	-	>0.1	-	

Table 3

The % conversion and % selectivity towards (3-phenyl propionaldehyde, cinnamyl alcohol and 3-phenyl propanol) of each catalyst form cinnamaldehyde.

	% Conversion	% Selectivity							
		3-Phenyl propionaldehyde	$PFF(s^{-1})$	Cinnamyl alcohol	$PFF(s^{-1})$	3-Phenyl propanol	$PFF(s^{-1})$	Cinnamic acid	$PFF(s^{-1})$
Pt/NP	52.6	9.9	1.80	67.2	12.26	22.9	4.19	>0.1	-
Pt/PEI/NP	98.1	>0.1	-	70.7	18.19	25.4	6.53	3.9	0.99
Pt/DFNS	68.0	0.3	0.33	44.4	49.61	50.0	55.85	5.3	5.91
Pt/PEI/DFNS	92.5	4.3	2.61	70.9	42.79	24.8	14.94	>0.1	-



Fig. 5. Graphic representation of the % selectivity and PFF (s⁻¹) toward the different products of the hydrogenation od cinnamaldehyde over each of the catalyst.

4. Conclusion

We have prepared Pt supported on nanosilica and DFNS, which either anchored directly on to the support or via a polyethylenimine (PEI) linker. The PEI linker increase the Pt-loading on the supports up to 16 times than direct binding. These catalysts displayed 100% conversion for the hydrogenation of cyclohexene to cyclohexane. For the hydrogenation of benzaldehyde, a conversion of upto 62.9% was obtained with a selectivity of 73.4% towards the formation of benzyl alcohol for Pt/PEI/DFNS, with a PFF of 52.9 s⁻¹. The formation of benzoic acid was observed in same catalytic reaction, which is attributed to the presence of small amount of water, resulting in the classical hydration to form a germinal diol, followed by dehydration to benzoic acid. The Pt/PEI/NP catalyst resulted in a high conversion of 98.1% for the hydrogenation of cinnamaldehyde. This catalyst was 70.7% selective towards cinnamyl aldehyde, 25.4% selective towards the formation of 3-phenyl propanol with a PFF 18.9 s^{-1} after 6 h. Since no 3-phenyl propionaldehyde was formed, a shorter reaction time might lead to a higher conversion of cinnamyl aldehyde. In a similar type of hydration, followed by dehydration, cinnamic acid was produced in small quantities.

CRediT authorship contribution statement

Z. Xantini: Investigation. **E. Erasmus:** Conceptualization, Validation, Formal analysis, Resources, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] M. Dhiman, V. Polshettiwar, J. Mater. Chem. A 4 (2016) 12416-12426.
- [2] J. Niemantsverdriet, Appl. Surf. Sci. 144–145 (1999) 366–374.
- [3] V. Lordi, N. Yao, J. Wei, Chem. Mater. 13 (2001) 733–737.
- E. Finocchio, E. Macis, R. Raiteri, G. Busca, Langmuir 23 (2007) 2505–2509.
 M.A. Bodaghifard, H. Moghanian, A. Mobinikhaledi, F. Esmaeilzadeh, Inorg. Nano-Metal Chem. 47 (2017) 845–849.
- [6] E. Erasmus, P.C. Thüne, M.W.G.M. Verhoeven, J.W. Niemantsverdriet, J.C. Swarts, Catal. Commun. 27 (2012) 193–199.
- [7] J. Xie, Y. Wang, Y. Li, Y. Wei, Springer. 102 (2011) 143-154.
- [8] S. Dwivedi, S.S. Gujral, T. Taniike, M. Terano, Pure Appl. Chem. 85 (2012) 1–9.
 [9] X. Tu, Z. Li, J. Lu, Y. Zhang, G. Yin, W. Wang, D. He, RSC Advances. 8 (2018) 2887–2891.
- [10] G.L. Witucki, J. Coat. Technol. 65 (1993) 57-60.
- [11] W. Huang, J.N. Kuhn, C. Tsung, Y. Zhang, S.E. Habas, P. Yang, G.A. Somorjai, Am. Chem. Soc. 8 (2008) 2027–2034.
- [12] P. Gautam, M. Dhiman, V. Polshettiwar, B.M. Bhanage, R. Soc. Chem. 18 (2016) 5890-5899.
- [13] E. Erasmus, J.W. Niemantsverdriet, J.C. Swarts, Langmuir 28 (2012) 16477-16484.
- [14] S.B. Kalidindi, B.R. Jagirdar, ChemSuSChem 5 (2012) 65-75.
- [15] J. Haber, Pure & Appl. Chem. 63 (1991) 1227–1246.
- [16] B.G. Trewyn, S. Giri, I.I. Slowing, V.S.Y. Lin, Chem. Commun. (2007) 3236–3245.
- [17] Y. Xia, B. Gates, Y. Yin, Y. Lu, Adv. Mater. 12 (2000) 693–713.
- [18] J.L. Gole, Z.L. Wang, Z.R. Dai, J. Stout, M. White, Colloid Polym. Sci. 281 (2003) 673-685.
- [19] S.M. Sadeghzadeh, R. Zhiani, M. Khoobi, S. Emrani, Micropor Mesopor Mater. 257 (2018) 174–1153.
- [20] M.J. Ortiz-Iniesta, H.J. Heeres, I. Melian-Cabrera, Micropor Mesopor Mater. 171 (2013) 208–214.
- [21] Y. He, A. Jawad, X. Li, M. Atanga, F. Rezaei, A.A. Rownaghi, J. Catal. 341 (2016) 149–159.
- [22] S.M. Sadeghzadeh, R. Zhiani, M. Khoobi, S. Emrani, Micropor Mesopor Mater. 257 (2018) 147–153.
- [23] A. Maity, V. Polshettiwar, ChemSusChem. 10 (2017) 3866-3913.
- [24] B. Singh, V. Polshettiwar, J. Mater. Chem. A (2016) 1–15.
 [25] M. Dhiman, B. Chalke, V. Polshettiwar, ACS Sustain. Chem. Eng. 3 (2015) 3224–
- 3230.
- [26] C. D. Seaborn and F. H. Nielsen, Biological Trace Element Research., 3, 251-261. [27] D.S. Moon, J.K. Lee, Langmuir, 28 (2012) 12341–12347
- [27] D.S. Moon, J.K. Lee, Langmuir. 28 (2012) 12341–12347.
 [28] V.V. Pushkarev, Z. Zhu, K. An, A. Hervier, G.A. Somorjai, Top Catal. 55 (2012)
- 1257–1275.
- [29] K. Niknam, A. Deris, F. Panahi, Chin. J. Catal. 34 (2013) 718–722.
- [30] X. Zhai, Y. Pan, J. Xu, A. Wang, S. Wu, J. Shen, RSC Adv. 5 (2015) 105855– 105861.
- [31] D. Xia, J. Quan, G. Wu, X. Liu, Z. Zhang, H. Ji, D. Chen, L. Zhang, Y. Wang, S. Yi, Y. Zhou, Y. Gau, R. Jin, Nanomaterials 9 (2019) 1225.
- [32] M. Englisch, A. Jentys, J.A. Lercher, J. Catal. 166 (1997) 25-35.
- [33] J. Dai, M.L. Bruening, Nano Lett. 2 (2002) 497–501.
- [34] E.M.E. van Kimmenade, A.E.T. Kuiper, Y. Tamminga, P.C. Thune, J.W. Niemantsverdriet, J. Catal. 223 (2004) 134–141.

Z. Xantini and E. Erasmus

- [35] F.A. Cotton, G. Wilkinson, P.L. Gaus, Basic Inorganic Chemistry, 3rd Ed., John Wiley & Sons Inc, United States, 1976.
- [36] V.I. Okafor, N.J. Coville, S. Afr, J. Sci. 95 (1999) 503-508.
- [37] W. Yu, M.D. Porosoff, J.G. Chen, Chem. Rev. 112 (2012) 5780–5817.
- [38] C. Lian, H. Liu, C. Xiao, W. Yang, K. Zhang, Y. Liu, Y. Wang, Chem. Commun. 48 (2012) 3124–3126.
- [39] Z.X. Chen, G.C. Smith, C.A.J. Putman, E.J.M. ter Voert, Catal. Letters. 50 (1998) 49–57.
- [40] N. Magqi, Preparation, characterization and selective hydrocarbon transformation applications of flat-model and zeolite supported catalysts PhD thesis, University of the Free State, Bloemfontein, 2014.
- [41] F. Zaera, ACS Catal. 7 (2017) 4947–4967.
- [42] K. Kaviyarasu, E. Manikandan, Z.Y. Nuru, M. Maaza, Mater. Lett. 160 (2015) 61-63.
- [43] P. Gallezot, D. Richard, Catal. Rev. Sci. Eng. 40 (1998) 81.
- [44] Y. Yuan, S. Yao, M. Wang, S. Lou, N. Yan, Curr. Org. Chem. 17 (2013) 400.
- [45] L.K. Parrott, E. Erasmus, Catal. Lett. 48 (2018) 2008–2018.
- [46] E. Botha, M. Landman, P.H. van Rooyen, E. Erasmus, Inorg. Chim. Acta 482 (2018) 514–521.
- [47] E. Erasmus, J. Elec. Spec. Rel. Phenom. 223 (2018) 84–88.
- [48] S.J. Gerber, E. Erasmus, Mater. Chem. Phys. 203 (2018) 73-81.
- [49] S.J. Gerber, E. Erasmus, Trans. Metal Chem. 43 (2018) 409–420.
- [50] Z. Dong, X. Le, X Li, W. Zhang, C. Dong and J. Mia, Appl. Catal. B, Enviro. 2014, 158-159, 135-159.
- [51] N. Bayal, B. Singh, R. Singh, V. Poahettiwar, Sci. Rep. 6 (2016) 1–11.
 [52] V. Polshettiwar, D. Cha, X. Zhang and J.M. Basset., Angew.Chem.Int.Ed., 2010, 49, 9652-9656.

- [53] A. Mobinikhaledi, H. Moghanian, S. Pakdel, Chin. Chem. Lett. 26 (2015) 557– 563.
- [54] M. Yamaura, R.L. Camilo, L.C. Sampaio, M.A. Macedo, M. Nakamura, H.E. Toma, J. Magn. Magn. Mater. 279 (2004) 210–217.
- [55] R.A. Bini, R.F.C. Marques, F.J. Santos, J.A. Chaker, J. Magnet. Magnet. Mater. 324 (2012) 534–539.
- [56] H. Kanno, Mater. Sci. Eng. Carbon (2016) 153–171.
- [57] C. Lee, Y. Hyun, J. Choi, Carbon Nano-Objects. (2019) 225-242.
- [58] K. Zhu, C. Chen, Interf. Sci. Technol. (2019) 281–330.
- [59] F.B. Li, X.Z. Li, Chemosphere 48 (2002) 1103–1111.
- [60] R. Fu, H. Zeng, Y. Lu, S.Y. Lai, W.H. Chan, F. Ng, Carbon 33 (1995) 657-661.
- [61] G. Zhang, D. Yang, E. Sacher, J. Phys. Chem. C 111 (2007) 565–570.
- [62] S.M. Kim, Y.S. Kim, D.W. Kim, J.W. Yang, Green Chem. (2012) 2996–2998.
- [63] P. Ferreira, A. Hern Andez-Ortega, B.B. Herguedas, J. Rencoret, A. Guti Errez, M. Martinez, J. Jimez-barbero, M. Medina, A.T. Mertinez, Biochem. J. 425 (2010) 585–593.
- [64] N. Magqi, Preparation, characterization and selective hydrocarbon transformation applications of flat-model and zeolite –supported catalyst PhD thesis, University of the Free State, Bloemfontein, 2014.
- [65] R.M.B. Basale, Selective catalytic hydrogenation of,-unsaturated aldehyde to unsaturated alcohol: investigation of the role of the promoter, Eindhoven University of Technology, Netherlands, 2013.
- [66] H. Liu, Q. Mei, S. Li, Y. Yang, Y. Wang, H. Liu, L. Zheng, P. An, J. Zhang, B. Han, Chem. Commun. 54 (2018) 908–911.
- [67] C. Mohr, P. Claus, Sci. Progr. 84 (2001) 311.
- [68] T. Mallat, Z. Bodnar, P. Hug, A. Baiker, J. Catal. 153 (1995) 131–143.
- [69] T. Mallat, A. Baiker, Chem. Rev. 104 (2004) 3037-3058.