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The vapour phase hydrogenation of cinnamaldehyde using cobalt supported inside and outside hollow carbon spheres

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Draft

Abstract

The hydrogenation of cinnamaldehyde is usually performed in the liquid phase in batch mode. In this study, a vapour phase flow system has been used to evaluate the use of cobalt catalysts supported inside and outside hollow carbon spheres (HCSs). The influence of temperature, hydrogen flow rate and catalyst mass on the hydrogenation reaction was investigated. The catalysts generally showed modest conversion to the required products, hydrocinnamaldehyde, 3-phenyl propanol, cinnamyl alcohol together with formation of various decomposition products. The data revealed that the Co@HCS showed better conversion and product selectivity compared to the Co/HCS. The catalysts with smaller particle sizes (ca. 6 nm) were more efficient than big particles (30 – 40 nm). An increase in reaction temperature (200 – 300°C) resulted in a lower cinnamaldehyde conversion and a poor product selectivity. TPR studies revealed that the Co@HCSs had a stronger metal-support interaction than the Co/HCSs catalysts. Catalyst recycling studies revealed that only the Co/HCSs could be regenerated (4 cycles) and post reaction analysis of the catalysts revealed that this was due to HCS pore blockage and not Co sintering.

Keywords: Hollow carbon spheres; hydrogenation; cinnamaldehyde; cobalt; catalysis

Graphic abstract

1. Introduction

Cinnamaldehyde (CALD) belongs to the family of α,β -unsaturated aldehydes. Hydrogenation of CALD is an industrially important reaction, involving selective catalytic reduction of $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds in the presence of molecular hydrogen^{1,2}. The reaction produces three main compounds, which are, hydrocinnamaldehyde (HCALD), hydrocinnamyl alcohol (3-phenyl propanol, 3PP) and cinnamyl alcohol (CAL) (Scheme 1)³. HCALD is produced when the $\text{C}=\text{C}$ bond is selectively reduced, CAL is a product of the selective reduction of the $\text{C}=\text{O}$ bond and 3PP is a product of the reduction of both the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds⁴. Low molecular weight fragments and other high molecular weight compounds e.g. formaldehyde, styrene, and ethylbenzene can also be produced as by-products^{5,6}.

Scheme 1: Products of the catalytic hydrogenation of CALD

Selective reduction of the C=O bond of α,β unsaturated aldehydes is generally challenging as C=C bond reduction is thermodynamically favoured⁷ over C=O reduction⁸⁻¹⁰. An ideal catalyst for the hydrogenation of CALD would selectively produce one main unsaturated compound, with no unwanted by-products, at moderate temperature and pressure. Noble metal catalysts such as Pt, Ir, Os and Pd have been successfully used for the liquid phase hydrogenation reaction and have shown good catalytic activity and selectivity¹¹.

Transition metal catalysts such as Co, Ni and Cu are less expensive, more abundant and have shown good catalytic activity towards the hydrogenation of CALD^{5,9,12}. However, these catalysts also suffer from poor selectivity. Numerous approaches to enhance the catalyst activity/selectivity have been reported and they, include among others, the use of bimetallic catalysts¹³, variation of support properties and optimization of catalyst particle size and shape². Reaction conditions, such as, the amount of catalyst, temperature, pressure and solvent, also play an important role in the success of this hydrogenation process [8]. Most of these reactions have been done in the liquid phase using batch reactors but these liquid phase hydrogenation processes use large quantities of organic solvents¹⁴⁻¹⁸.

In the liquid phase hydrogenation of CALD, high activity and selectivity have been achieved with Co based catalysts. However, the reactions require high $H_2(g)$ pressures and long reaction

times due to the low activity of Co. In this study we have used a vapour phase approach to evaluate Co catalysts as this allows for the use of a flow system to generate the products. Interestingly, the vapour phase hydrogenation of cinnamaldehyde has not been widely investigated.

Reddy and co-workers⁹ reported on the vapour phase hydrogenation of CALD with bimetallic catalysts supported on silica. The catalysts' active metal phases included the alloys CoNi, NiCu, and CoCu. In their study it was shown that CoNi was highly selective towards HCALD while CoCu was highly selective towards CAL, reaching 45% yields. All the catalysts gave good conversion, above 60 %, and the NiCu catalyst gave the best conversion (75%). No by-products were reported at the optimal temperature used (270 °C). However, above 270 °C CALD fragmented products formed, indicating a decomposition of reactants and/or products. Chin and co-workers⁵ also reported on the vapour phase hydrogenation of CALD, using Ni catalysts supported on mesoporous silica. Optimal results were obtained at 300 °C, with up to 80% conversion and up to 80 % selectivity towards HCALD. 3PP was also produced, alongside styrene and ethylbenzene as by-products, CAL was not produced. In a study by Jao and co-workers⁴, the vapour phase hydrogenation of CALD with Ni supported on Si/MCM41 was investigated at 200 °C. Again, HCALD was produced in high yields (up to 60 %). Other products were 3PP, styrene and ethyl benzene but CAL was not produced. The above appear to be the only reports on studies that involve the vapour phase hydrogenation of CALD. No reports of Co on carbon supports have been described for the vapour phase hydrogenation of CALD.

Continuing from earlier studies by others working in our research group on the use of Co supported on carbon in catalysis¹⁹⁻²¹ we herein report on their use for the vapour phase CALD hydrogenation reaction using hollow carbon spheres (HCSs) as a support. HCSs contain a mesoporous shell that allows for the loading of Co both inside and outside HCSs; the structure can support a high loading of small metal nanoparticles. The encapsulation of metal nanoparticles inside HCSs can protect the metal from sintering, leaching and agglomeration during harsh catalytic reaction conditions²². The synthesized catalysts were named Co@HCSs and Co/HCSs for catalysts supported inside and outside HCSs, respectively. The Co@HCSs catalysts were synthesized by using two different types of templates, polystyrene (PS) and the co-polymer, PS-*b*-poly (acrylic acid) containing 8% acrylic acid (PS-*b*-PAA₈) and were named Co_xO_y@HCSs_PS and Co_xO_y@HCSs_PS-*b*-PAA₈, respectively²³. The PS-*b*-PAA₈ template contained functional groups that assisted with controlling and producing small metal

particles²³. The new Co/HCSs catalysts were synthesized using a PS-*b*-PAA₈ template [24]. Briefly, the PS-*b*-PAA₈ template was coated with a resorcinol formaldehyde (RF) carbon source and thereafter the template@RF composite was loaded with Co nanoparticles. Calcination under N₂ at high temperature led to the removal of the polymer template and pyrolysis of the RF led to the formation of Co nanoparticles loaded on the outside of HCSs. The effects of particle size, metal loading and the role of diffusion on Co loaded either inside or outside the HCSs, were investigated. The catalysts were further evaluated by varying the reaction temperature, H₂ flow rate and catalyst mass.

2. Materials and methods

2.1. Materials

Cinnamaldehyde (CALD) and tetrahydrofuran (THF) were purchased from Sigma Aldrich and used without further purification. The GC standards, cinnamyl alcohol (CAL), hydrocinnamaldehyde (HCALD) and 3-phenyl propanol (3PP) were also all purchased from Sigma Aldrich and used without further purification. Hydrogen gas (H₂ (g)) was purchased from Afrox South Africa and was passed through a gas filter before use.

2.2. Methods

The synthesis of the Co@HCSs catalysts and Co/HCSs catalysts has been previously described^{23,24}. The synthesized catalysts (100 – 500 mg) were reduced inside a down flow vertical fixed bed glass tube reactor (l = 42 cm, d = 2 cm). The reactor was placed inside an electrically heated vertical tube furnace equipped with a K-type thermocouple. Catalyst reduction was done at 350 °C for 2 h under 50 mL/min H₂ flow. The reduced catalyst (100 mg - 500 mg) inside the vertical tube reactor was cooled down to 200 °C and allowed to stabilize for 30 min. CALD (2.5 mL) dissolved in THF (6.25 mL) was injected into the reactor using an automatic syringe pump (SAGE instruments, model 341B) set at 1.5 mL h⁻¹. The CALD was injected over 5 h period under 100 mL/min H₂ flow and the reaction products were collected every hour. The reactor was connected to a glass sample collection tube (l = 6 cm, d = 2 cm) equipped with a glass tap. The sample collection tube was emptied every hour and the products were immediately diluted in THF and analysed with an offline GC-FID using a capillary column (Phenomenex Zebron, 30m x 0.53 mm I.D) and N₂ as a carrier gas. Pure chemical standards were used to identify the GC peaks. Catalyst recycling was done by re-oxidizing the reacted catalyst at 200 °C under flowing air at 50 mL/min for 1 h. The calcined catalyst was

weighed and placed inside the glass tube reactor, reduced and tested for vapour phase hydrogenation of CALD following the procedures mentioned above.

Temperature-programmed reduction (TPR) analysis was carried out with a Micromeritics Auto Chem II instrument. Approximately 70 mg of the catalyst was placed inside a quartz tube and pre-treated under helium (30 ml/min) at 150 °C for 30 minutes and cooled down to 50 °C. Thereafter, the catalyst was re-heated to 900 °C at a rate of 10 °C/min under 5% H_2 /Ar flowing at 50 mL/min. H_2 consumption was measured with a thermal conductivity detector (TCD). A Micromeritics Tristar 3000 surface area and porosity analyser was used to determine the surface area and pore volumes.

3. Results and discussions

3.1 Catalyst synthesis and characterization

The catalyst synthesis procedures have been reported in the literature^{23,24}. Catalysts with three Co loadings (inside and outside the HCSs) were studied (5%, 10%, 15%). Characterization data has been previously reported (metal loading, particle size and BET surface area) and the data is also given in Table S2 to provide easy access to key information^{23,24}. Similar Co metal particle sizes (5.4 to 6.6 nm) were obtained both inside and outside HCSs, for some of the catalysts, and this allowed for the direct comparison of their activities. The BET surface areas of the catalysts were also similar and therefore made it possible to compare the activity of the catalysts. The catalysts contained various Co and CoOx phases and prior to reaction all were reduced and converted to Co.

3.2 Temperature programmed reduction studies

Temperature programmed reduction (TPR) studies of the catalysts were performed to investigate the catalyst reducibility and the Co-carbon interactions. The TPR profile of the pristine HCSs prepared with a PS-b-PAA8 template can be found in Figure S1. No hydrogen adsorption was observed by the HCSs (< 300 °C) during the TPR experiment while H_2 consumption was observed above 400 °C is due to the gasification of the C support to form CH_4 ^{25,26}. The release of CH_4 is indicated by the negative peak appearing after 500 °C, with a maximum at 700 °C¹⁹.

Co_3O_4 is known to reduce to Co in a two-step process²⁷. The two peaks are normally expected at *ca.* 180 – 250 °C ($\text{Co}_3\text{O}_4 \rightarrow \text{CoO}$) and at *ca.* 250 - 450 °C ($\text{CoO} \rightarrow \text{Co}$) in the presence of

carbon supports. CH_4 formation occurs above 400 °C but this peak can overlap with the high T Co peak^{28,29}.

The TPR profiles of the three catalysts (Co@HCSs_PS , $\text{Co@HCSs_PS-b-PAA}_8$ and Co/HCSs) at three different Co loadings (5 %, 10%, 15%) are reported in Figure 1 and their peak positions in Table S1. It is to be noted that all the 5% loaded catalysts had similar Co sizes ($d = ca. 6 \text{ nm}$, Table S2)^{23,24}. At 10% and 15% Co loading the Co/HCSs and $\text{Co@HCSs_PS-b-PAA}_8$ catalysts contained small nanoparticles ($\sim 6 \text{ nm}$) while the Co@HCSs_PS catalysts contained larger particles ($>20 \text{ nm}$).

Figure 1: TPR profiles of the (A) 5%, (B) 10 % and (C) 15% loaded catalysts, (i) Co@HCSs_PS , (ii) $\text{Co@HCSs_PS-b-PAA}_8$ and (iii) Co/HCSs

Figure 1A shows the TPR profiles of the three 5% Co loaded catalysts and their peak positions are summarized in Table S1. Two major peaks (ca. 250-300 °C and 410-450 °C) related to the reduction of Co_3O_4 to Co are observed for all three catalysts. A small peak can also be seen in the three catalysts (ca. 180-220 °C) as well as a small peak for 5% Co@HCSs_PSPAA at ca. 350 °C; due to a second Co species that has been reduced. These peaks are more prominent in the TPR profiles of the 10% and 15% loaded catalysts (see Figures 1B and 1C). Peaks due to residual nitrate are not expected as the catalysts were heated to 600 °C during preparation. The two major peaks are associated with species showing strong Co-carbon interactions relative to the Co species associated with the minor peak(s). The 5% Co/HCSs catalyst had the lowest

reduction temperatures (254 and 410 °C) of the three catalysts, and that could relate to the effect of H₂ diffusion. The 5%Co@HCSs_PS had lower reduction temperatures (259 and 433 °C) than the 5%Co@HCSs_PSPAA (298 and 454 °C). This is an indication that stronger cobalt-to-support interactions occurred with the HCS created from PSPAA, caused by the functional groups on the PAA template that was used in the synthesis of the HCSs. Carbon methanation was observed above 400 °C, consistent with previous studies^{21,28}.

The TPR profiles for the 10% Co loaded catalysts are reported in Figure 1B and the data are like those for the 15% loaded catalysts shown in Figure 1C. For the 10%Co/HCSs catalyst two reduction peaks for the major Co species can be observed at 278 and 428 °C. The reduction peaks occurred at higher temperatures than observed for the 5%Co/HCSs catalyst, indicating the expected increase in reduction T with increasing Co loading. A minor species with peak at 191 °C was also noted and had increased in intensity (compare Figures Aiii and Biii); and increases further at 15% loading (Figure Ciii). The data was consistent with the minor species having a weaker interaction with the carbon and could be linked to larger Co particles.

The 10%Co@HCSs_PS-b-PAA (and 15% loading) catalyst behaved similarly to the Co/HCSs catalysts, but with different ratios of the two Co species. The two species had similar concentrations as reflected by peak heights for the four peaks at 176/351 °C and 266/413 °C (205/321 °C and 254/424 °C for the 15% loaded catalyst). The Co@HCSs catalysts had varying reduction temperatures relative to the Co/HCSs, which are related to diffusion effects and metal-to-support interactions.

The 10%Co@HCSs_PS catalyst has one major reduction peak at 360 °C (Figure Bi). This was associated with the presence of the large Co particles (38-45 nm). It has been previously reported by Luisetto et al³⁰ that the two cobalt oxide reduction steps can give one reduction peak in the presence of large cobalt particles (> 20 nm). A similar profile is seen for 15%Co@HCSs_PS (Figure Ci).

From this, and previous studies involving Co supported on carbon (where TPR analysis was performed) a reduction temperature of 350 °C was chosen to convert the Co₃O₄ on/in the HCS supports to Co, the active catalyst needed for the HCALD reduction reaction²¹.

3.3 Catalytic study

The catalytic study was carried out to explore the role of the location of the Co in/on a hollow carbon sphere (Co@HCS and Co/HCS) under conditions in which the Co loading, Co particle

size and Co mass were similar. A model reaction, the hydrogenation of cinnamaldehyde, using a flow system, was chosen for the study. This reaction can occur in the gas phase at ca. 200 °C and thus the Co loaded HCSs will be stable under these conditions. No attempt was made to optimize the reaction – established reaction conditions were used for the study as our focus was on elaborating the effect of placing catalysts inside the HCSs relative to placing the Co outside the HCSs. This study complements an earlier vapour phase study involving an *oxidation reaction* (liquid phase oxidation of benzaldehyde) in which Co_3O_4 catalysts were supported in/on HCSs²⁴.

Figure 2 shows the plot of the catalytic activity during 5 h of hydrogenation for all nine catalysts. It was observed that for all the catalysts that the CALD conversion (to all products) decreased as the reaction progressed. This indicates catalyst deactivation/poisoning with time, possibly caused by reaction of the Co with undesired by-products formed from CALD. It has been reported that undesired side reactions can lead to a loss of active sites in vapour phase hydrogenation reactions³¹. The loss of active sites in the gas phase hydrogenation reaction usually occurs through coke deposition on the catalyst surface³². As expected, the CALD conversion showed a dependence on metal loading, particle size and location of the Co in/on the HCS; this issue is discussed in further detail in a later section.

Figure 2: Catalytic activity of the catalysts during 5 h hydrogenation of CALD with (a) 5%Co@HCSs_PS, (b) 5%Co@HCSs_PS-b-PAA₈, (c) 5%Co/HCSs, (d) 10%Co@HCSs_PS, (e) 10%Co@HCSs_PS-b-PAA₈, (f) 10%Co/HCSs, (g) 15%Co@HCSs_PS, (h)

15%Co@HCSs_PS-b-PAA₈ and (i) 15%Co/HCSs. Reaction conditions: 100 mg catalyst at 200 °C, 100 mL/min H₂ flow rate and 1.5 mL/min CALD flow rate.

Table 1: Conversion, activity and selectivity after 1 h hydrogenation of CALD with the catalysts ^a.

Catalyst	CALD Conv (%)	Activity (mol _{CALD} h ⁻¹ g _{Co} ⁻¹) x10 ⁻³	Product Selectivity (%)			
			HCALD	3PP	CAL	Other
5%Co@HCSs_PS	2.6	19	38.3	61.7	-	-
5%Co@HCSs_PS-b-PAA ₈	7.2	53	30.5	38	27.3	4.2
5%Co/HCSs	1	0	-	100	-	-
10%Co@HCSs_PS	10.3	29	17.7	28.3	-	54.0
10%Co@HCSs_PS-b-PAA ₈	74.8	231	13.6	37.7	2.1	46.6
10%Co/HCSs	59.8	214	15.2	21.0	3.5	60.3
15%Co@HCSs_PS	1.3	2.7	100	-	-	-
15%Co@HCSs_PS-b-PAA ₈	99.7	207	16.7	48.8	9.4	25.1
15%Co/HCSs	80.5	211	12.1	23.1	-	64.8

^a Reaction conditions: 100 mg catalyst at 200 °C, 100 mL/min H₂ flow rate and 1.5 mL/min CALD flow rate.

Table 1 reports the selectivity, catalytic activity as well as the conversion of CALD for the nine catalysts after 1 h of hydrogenation of CALD at 200 °C. Hydrocinnamaldehyde (HCALD), 3-phenyl propanol (3PP) and cinnamyl alcohol (CAL) were all produced alongside other low molecular weight products. These latter products have been lumped together and termed ‘other’ as they were not the target products of this study.

3.3.1 Effect of the hydrogen flow rate

The 10%Co@HCSs_PS-b-PAA₈ catalyst was used to investigate the effect of varying the H₂ flow rate (50 mL/min, 100 mL/min and 150 mL/min), while keeping the temperature (200 °C) and catalyst mass (100 mg) constant. No CALD conversion was observed at 50 mL/min and 150 mL/min. Varying the flow rate of H₂ can change the partial pressure of the reactants. This may result in a competition between the reactants (H₂, CALD) for the same adsorption sites on the catalyst surface, and this could result in decreased catalytic activity in the presence of an

increase in H_2 on the Co surface³⁸⁻⁴⁰. The increase in H_2 on the surface could also lead to over reduction of CALD. Furthermore, an increase in CALD concentration may also result to a rapid catalyst deactivation due to formation of polymerization products.

3.3.2 Effect of reaction temperature

Blank reactions were carried out at 200 and 300 °C using HCSs that did not contain any metal. CALD was passed through the reactor using a flow of H_2 (100 ml/min). There was no CALD conversion observed at both 200 and 300 °C. This indicated that any product formation observed was due to the Co nanoparticles.

The 10%Co@HCSs_PS-b-PAA₈ catalyst was also used to investigate the effect of the reaction temperature (150 °C, 200 °C, 250 °C, 300 °C) on the CALD conversion while keeping the H_2 flow rate (100 mL/min) and catalyst mass (100 mg) constant. The conversion data are reported in Figure 3A. At 150 °C there was no conversion observed over 5 h of reaction; reaction was only observed above 200 °C. As the temperature was increased from 200 to 250 and 300 °C, the conversion however, decreased, viz. after 1 h from 74.8 to 37.1 to 25% (Figure 3A). This can be attributed to the poorer adsorption of reactant molecules with temperature^{29,33} or to the accelerated deactivation of the catalyst at higher temperatures.

Figure 3B shows the product *selectivity* at 25% conversion at the three different temperatures. It was observed that an increase in reaction temperature led to poor product selectivity to the desired products (HCALD, CAL). Instead, large quantities of the low molecular weight by-products were produced due (possibly) to the decomposition of CALD at the high temperatures⁹. The best results, in terms of CAL/HCALD yields, were obtained at 200 °C, but even here over reduction of the 3PP was observed. At higher temperatures large amounts of ‘other’ products were formed, which suggested that products readily breakdown at these temperatures.

Figure 3: (A) Conversion of CALD during 5 h of hydrogenation over 10%Co@HCSs_PS-b-PAA₈ at different reaction temperatures. (B) Selectivity at 25% conversion of CALD over 10%Co@HCSs_PS-b-PAA₈ at different reaction temperatures. Reaction conditions: 100 mg catalyst, 100 mL/min H₂ flow rate and 1.5 mL/min CALD flow rate.

3.3.3 Effect of the amount of catalyst

The 10%Co/HCSs catalyst was used to investigate the effect of the amount of catalyst (100 mg, 200 mg, 300 mg, and 500 mg) on the reaction (200 °C; H₂ flow rate of 100 mL/min) and the results are shown in Figure 4. After 1 h, using the smaller amounts of catalyst (100 and 200 mg) only ca. 60% conversion was achieved, and the conversion dropped with increasing time. Increasing the catalyst content to 300 and 500 mg, the conversion reached 100 % and decreased with time³².

Figure 4B shows the product selectivity when using different amounts of 10%Co/HCSs. The data indicated poor selectivity for the desired product with increased amount of catalyst – over reaction is evident and large quantities of unwanted by-products were produced. Figure 5 further shows the product distribution after every hour, for 5 h, when using 300 mg and 500 mg catalysts. It was observed that over time the amount of the by-products formed was reduced, while the amount of HCALD and 3PP increased. This indicates that as the catalyst was poisoned the products were less liable to be over hydrogenated. Similar results were reported by Chin et al.⁵ when a 10%Ni/alumina catalyst was evaluated for the hydrogenation of CALD at 300 °C. They also noted that the conversion increased with increasing contact time. The catalyst selectively produced HCALD in large quantities, and the yield increased with increasing contact time until it reached a maximum and then decreased. The drop in HCALD yield was accompanied by the formation of high yields of side-products (ethyl benzene and phenyl-propanol).

Figure 4: (A) Conversion of CALD during 5 h of hydrogenation over 10%Co/HCSs using different amounts of catalyst and, (B) Selectivity after 1 h of hydrogenation of CALD with different amounts of catalyst.

Figure 5: Selectivity during 5 h hydrogenation of CALD with (A) 300 mg, and (B) 500 mg of 10%Co/HCSs

3.3.4 Effect of particle size

The use of two templates, polystyrene (PS) and polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA₈) resulted in the synthesis of Co@HCSs with variable particle sizes at similar metal loadings²³. This allowed for the effect of metal particle size to be investigated for the catalysts supported inside the HCSs. The PS template gave larger particles with TEM average diameters of 6.1, 38, and 44 nm (Table S1²³) for the 5%, 10% and 15% Co loaded catalysts, respectively. In contrast, the PS-*b*-PAA₈ template gave smaller particles with average diameters of 5.4, 5.8 and 6.6 nm (Table S1²³) for the 5%, 10% and 15% Co loaded catalysts, respectively.

The large particles (Co@HCSs_{PS}) gave low conversion and there were no significant improvements with increased metal loading (Table 1). The CALD conversion increased from 2.6 to 10.3 % as the metal loading increased from 5 % to 10 % Co. As the metal loading

increased from 10% to 15% Co, the conversion decreased from 10.3 % to 1.3 % due to the increase in particle size. The small particles (Co@HCSs_PS-b-PAA₈) gave a high conversion, which increased with increasing metal loading. The conversion of CALD increased from 7.2 to 74.8 and 99.7 % as the catalyst loading increased from 5 to 10 and 15% Co.

The corresponding activity data ($\text{mol}_{\text{CALD}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{Co}}^{-1}$; Table 1) showed that the catalysts made from the PS template were 90% less active than those made from the PS-b-PAA template. Therefore, smaller particles are more efficient in the hydrogenation of CALD. A similar observation can be found in the study by Durndell and co-workers¹⁰, where the conversion of CALD with Pt catalysts of different sizes dropped drastically with increasing particle size, due to a reduction in active surface area. The particle size can also affect the geometric and electronic characteristics of the catalyst that would influence the adsorption and desorption behaviour of the reactants¹⁴. Therefore, the careful control of the metal particle size is important in the hydrogenation of CALD.

3.3.5 Comparison of the catalytic properties of Co@HCSs_PS-b-PAA₈ and Co/HCSs

Both Co@HCSs_PS-b-PAA₈ and Co/HCSs catalysts had similar loadings (5%, 10%, 15%) and Co particle sizes (*ca.* 6 nm) (Table S2²³). This allowed for the effect of placing the Co both inside and outside the HCSs to be studied. The catalytic behaviour of the 6 catalysts were compared under equivalent reaction conditions (100 mg catalyst, 100 mL/min H₂ flow rate and 1.5 mL/min CALD flow rate at 200 °C) and the selectivity data are shown in Figure 6, and the conversion data is summarized in Table 1.

- At 5% loading the Co/HCSs catalyst did not show any CALD conversion for the first 2 h of reaction. A conversion of 1% was observed after 3 h and remained at 1% for the remaining 5 h. It was evident that this catalyst was not active, even though it contained small active metal particles (6.2 nm).
- As the loading was increased to 10% and 15% Co, the conversion for the Co@HCSs catalysts increased to 74.8% and 99.8% respectively. These were higher than the conversions obtained with the Co/HCSs catalysts (59.8 % and 80.5 % for the 10% and 15% loaded catalysts, respectively). It was thus concluded that the encapsulation of the metal nanoparticles inside the HCSs enhanced the catalytic activity of the cobalt catalysts. In a study by Dong and co-workers²² the catalytic activities of PdCu catalysts supported inside and outside HCSs were investigated in liquid phase reactions. They

investigated the void confinement effects and realized that mass transfer limits were not significant for hydrogenation of small molecules such as styrene but became important with big molecules that could not pass through the pores (0.6 nm) of the HCSs. Both the PdCu@HCSs and PdCu/HCSs showed similar activity for hydrogenation of small molecules. In our study the catalysts contained pores with diameters of *ca.* 5 nm. These were big enough to eliminate mass transfer limitations. Reactant accumulation effects can also be eliminated as the reaction was done at 200 °C. The different catalytic activities could be due to the strong metal-support interactions that were confirmed by TPR in the Co@HCSs_PS-b-PAA8 catalysts. This is suspected because the metal support interactions may have allowed for better electron transfer between the carbon and Co.

- At 5% loading, the Co/HCSs (Figure 6 (ii)) catalyst showed very low conversion and produced only 3PP. At 10% loading ((iv)), HCALD, 3PP and CAL were all produced, with high selectivity towards 3PP (21 %) while producing 60% of the ‘other’ by-products. At 15% loading ((vi)) CAL was not produced and a large quantity of the unwanted by-products (65 %) was produced. Over-hydrogenation occurs when the Co is placed outside the HCSs under the reaction conditions used.
- At 5% loading, the Co@HCSs_PS-b-PAA₈ ((i)) catalyst produced smaller amounts of the unidentified by-products (4 %), while producing similar amounts of HCALD (30%), 3PP (38%) and CAL (27 %). At higher metal loadings (10 and 15 %), the amount of the unidentified by-products increased significantly and the selectivity towards CAL decreased. This could be due to the high activity of the high metal-loaded catalysts which resulted in excess hydrogenation of the CALD. It was further noted that the 15%Co@HCSs catalyst gave a higher conversion and better product selectivity when compared to the 10%Co@HCSs catalyst. It was also evident that the Co@HCSs catalysts showed better selectivity than the Co/HCSs catalysts as they produced less by-products. Wang and co-workers¹⁴ have reported that steric effects have an influence on catalyst selectivity, and this can be achieved by using core-shell catalysts as well as controlling metal particle diameter.
- All catalysts showed deactivation as the reaction proceeded (Figure 2). The relative deactivation rates between 1 h and 2 h gave the ordering: 15%Co/HCSs (1) > 10%Co/HCSs (0.9) > 10%Co@HCSs_PS-b-PAA₈ (0.7) > 15%Co@HCSs_PS-b-PAA₈ (0.4) (relative rates in brackets)) This ordering could be related to the high

concentration of unwanted by-products produced by the Co/HCSs as these by-products could poison the catalysts.

To briefly summarize the experimental work, the catalysts studied generally showed an increase in initial conversion as the metal loading increased, due to the increase in catalytically active metal surface area.

Table S5 shows the data obtained from other studies on the *vapour phase* hydrogenation of cinnamaldehyde with transition metal catalysts. In the studies by Jao et al.⁴ and Chin et al.⁵ it can be observed that the conversion decreased with increasing reaction time, as seen in our study. In both reports, the conversion at 15 min was higher than the conversion at 75 min⁵ and 105 min⁴, presumably due to catalyst deactivation. The reaction conditions in the study by Jao et al.⁴ are similar to those used in our study (200 °C ; 15% loading) but with 12 nm Ni particles. The conversion data (99.5 and 96.6 % CALD at 15 and 105 min) is comparable to our findings, where a conversion of 99.7 % was obtained after 60 min with 6.6 nm Co particles (15% loading). However, the selectivity data were different in the two studies. A selectivity of 51 % and 33.8 % towards unwanted by-products was obtained by Jao et al.⁴, while in our study only 25% selectivity to unwanted by-products was obtained. The differences in selectivity is related to both the different particle sizes and/or different metals used.

The two studies generally showed high formation of unwanted by-products, but in the study by Reddy et al.⁹ using bimetallic catalysts only trace amounts of by-products were reported. It is also worth noting that Reddy et al.⁹ reported 44% selectivity to cinnamyl alcohol when using a 10% CuCo bimetallic catalyst with 75% conversion. However, cinnamyl alcohol was not produced when using CoNi or NiCu catalysts. In our study, only 2% cinnamyl alcohol was produced with a 10% Co catalyst and 9% was produced with a 15% Co catalyst.

The TEM images of the reacted 5% and 10% catalyst are shown in Figures S2 and S3. The catalysts did not show sintering after 5 h of reaction and the particle sizes were still in the range of 5 – 6 nm.

Figure 6: Selectivity after 1 h hydrogenation of CALD with (i) 5%Co@HCSs_PS-b-PAA₈, (ii) 5%Co/HCS, (iii) 10%Co@HCSs_PS-b-PAA₈, (iv) 10%Co/HCSs, (v) 15%Co@HCSs_PS-b-PAA₈ and (vi) 15%Co/HCSs

3.3.6 Catalyst recycling

Figure 7 shows the catalytic activity and selectivity after 5 cycles of hydrogenation with 10%Co/HCSs. The catalyst still showed 80 % conversion after the third reaction cycle. On cycles 4 and 5, the conversion dropped to 65 and 25%, respectively. The data indicates that a major loss in activity only occurred after 4 reaction cycles. The stability of our catalysts was comparable to other catalysts previously reported in the literature^{18,36}. The TEM image and particle size distribution curve of the catalyst after 5 cycles can be found in Figure S4. No sintering was observed as the particle size was found to be 5.3 nm (initial particle size was 5.2 nm) (Table S2). The selectivity of the catalyst to HCALD was enhanced over the 5 cycles.

Figure 7: (A) Catalytic activity of 10%Co/HCSs during 5 cycles of 5 h hydrogenation of CALD and (B) selectivity at 1 h of hydrogenation of CALD with 10%Co/HCSs

The 10%Co@HCSs_PS-b-PAA₈ catalyst was also recycled, however the catalyst activity could not be recovered, due to pore blockage. The recyclability of the 10%Co@HCSs_PS-b-PAA₈ catalyst was tested with a fresh catalyst (300 mg; standard conditions; 5 h reaction). After use, the catalyst was calcined at 200 °C for 1 h, under flowing air at 200 °C. The catalyst was then re-used for the hydrogenation of CALD, however, less than 5% CALD was converted. The catalyst was then calcined at 220 °C for 2 h and reused. Up to 45 % conversion of CALD was obtained. After this, the catalyst was again calcined (220 °C; 5 h) and reused for the hydrogenation of CALD, but without improvement. Unfortunately, the calcination could not be performed above 220 °C because the carbon would decompose in the presence of oxygen and cobalt. The TGA analysis performed in air can be found in the supplementary information Figure S7, showing the onset of degradation at 230 °C.

Surface area analysis were done on the reused Co/HCSs and Co@HCSs catalysts after 5 and 4 uses, respectively. The used catalysts were calcined at 200 °C for 1h prior to the surface area analysis. The BET surface area, pore diameters and pore volumes of the catalysts are reported in Table S3. The corresponding BET isotherms and pore size distribution curves are reported on Figures S5 and S6, respectively. The surface area of both catalysts decreased significantly after the hydrogenation reaction, indicating a blockage of pores. The surface area of the 10%Co/HCSs catalyst decreased from 530 m²/g to 95 m²/g, and the 10%Co@HCSs_PS-b-PAA₈ decreased from 433 m²/g to 108 m²/g. For the Co/HCSs catalyst the blockage of pores does not have a negative impact on the catalytic activity as the catalysts could be recycled with recovery of the catalyst activity. With the Co@HCSs catalysts, the pores are very important

for the transportation of reactants to the inside of the HCSs, where the active metal nanoparticles are situated. The blockage of pores meant that the CALD could not reach the Co nanoparticles inside the HCSs, and as a result the catalyst could not be recycled.

4. Conclusion

The Co@HCSs and Co/HCSs catalysts prepared were analysed by TPR studies and it was shown that the reducibility of the different catalysts varied based on the location of the Co due to diffusion and metal-support interaction effects. The catalysts were evaluated for activity in the vapour phase hydrogenation of CALD and conversion was observed for most of the catalysts. The data showed evidence of catalyst deactivation by poisoning/coke deposition due to the formation of by-products. A variation in the rate of hydrogen flow showed that the amount of hydrogen has a significant influence on the reaction as it competes for adsorption sites with CALD. Reaction temperature studies indicated that a moderate temperature gave the best results. Furthermore, high reaction temperatures resulted in poor selectivity due to over-hydrogenation and decomposition of the reactants and products. A similar effect was observed with an increase in catalyst mass, where higher amounts of catalyst led to over-hydrogenation and large amounts of unwanted by-products due to an increase in contact time. Careful control of particle size was required to achieve optimum results in hydrogenation reactions as larger particles gave very low activity compared to smaller particles. Better conversion and selectivity were obtained with Co@HCSs than the Co/HCSs. However, an unexpected disadvantage of using Co@HCSs was the recyclability of the catalyst which was hindered by pore-blockage. The Co/HCSs catalysts could be recycled with up to 80% recovery of conversion. Surface area analysis showed that the pores of the HCSs were blocked during the reaction, and this had a negative impact on recyclability of the Co@HCSs catalysts as they depended on the pores as conduits for reactants and products to and from the active catalyst.

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