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### Short Communication

# Effect of particle size on selective hydrogenation of cinnamaldehyde by Pt encapsulated in mesoporous silica

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#### ABSTRACT

Pt nanoparticles of various sizes, viz. 8, 4.9, 3.6 and 1.8 nm were encapsulated in 2D hexagonal mesoporous silica by in-situ synthesis as well as post synthetic modifications so that the final catalyst composition was  $\leq 1$  wt.% Pt/SiO<sub>2</sub>. A kinetic analysis of the effect of particle size on selective hydrogenation of cinnamaldehyde was carried out on these catalysts. It was found that the materials, even at such low loading of Pt, were very active for the hydrogenation and selective for the desired product, cinnamyl alcohol. Among the different particle sizes, selectivity was found to be the highest on 8 nm particles. Kinetic analysis shows that the reaction follows a consecutive reaction pathway.

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## 1. Introduction

Oxide supported noble metal nanoparticles have long played a pivotal role in industrial catalysis [1,2]. The unique advantage of such catalysts is that activity and selectivity can be fine tuned by controlling the particle size and shape since active centres in metal nanoparticles are present on the surface and the surface features of metal nanoparticles change with shape and size [3,4]. This variation in catalytic activity with changing particle size and shape is because of the various molecular scale factors which include changes in surface structure, electronic state, metal–support interaction and oxidation states, especially in the range of 1–10 nm [5,6].

Selective catalytic hydrogenation of organic substrates containing a number of unsaturated functional groups is such a process which shows marked influence by particle size variations. Moreover, this is an important step in industrial production of fine chemicals, especially the selective hydrogenation of  $\alpha$ , $\beta$ -unsaturated carbonyls like cinnamaldehyde, which is crucial in the manufacture of pharmaceuticals, flavours and fragrances [7,8]. The desired reaction viz., chemoselective hydrogenation of carbonyl bond in multi-unsaturated aldehydes and ketones is a difficult task since thermodynamics favours C=C hydrogenation over C=O by ca. 35 kJ/mol [9]. It is reported that adsorption energies of C=C and C=O bonds on various crystal planes of metal particles are different and this can be exploited for improving the selectivity of the catalyst [10,11]. Since nature of crystal planes exposed on the nanoparticle surface

changes with variations in particle size, we expect a reflection of this on the selectivity of various products. Hence it is imperative that the active nanoparticles are as monodisperse as possible and with least tendency for agglomeration and change in particle size during reactions. Conventional methods of catalyst preparations have the drawback of non uniform particle sizes which severely affects the selectivity to desired product. We have recently developed a simple in-situ method for encapsulating monodisperse nanoparticles within the channels of mesoporous silica [12,13]. Such catalysts with uniform sized Pt nanoparticles isolated exclusively within the channels of mesoporous compounds can be considered to be good candidates for size sensitive reactions due to monodispersity as well as stability. We have selected a series of catalysts with Pt nanoparticles of varying sizes encapsulated in mesoporous silica to study the effect of particle size on selective hydrogenation. In this paper, we report the hydrogenation of cinnamaldehyde on Pt nanoparticles of sizes 8, 4.9, 3.6 and 1.8 nm encapsulated in 2D hexagonal mesoporous silica and kinetic analysis to understand the reaction pathways.

#### 2. Experimental

#### 2.1. Synthesis of Pt/mSiO<sub>2</sub>

Pt particles with average sizes of 1.8 and 3.6 nm were synthesised by alcohol reduction method and incorporated in the channels of mesoporous SBA-15 by sonication as reported elsewhere [14]. In situ method as reported by us [12,13] was followed for the synthesis of Pt with average sizes of 8 and 4.9 nm encapsulated in mesoporous

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silica (Supplementary material). Pt wt.% of the catalysts with 1.8, 3.6, 4.9 and 8 nm Pt particles were found to be 0.96, 1, 0.72 and 0.7 wt.% of Pt respectively, by elemental analysis.

#### 2.2. Cinnamaldehyde hydrogenation

A 100 mL Parr autoclave equipped with a pressure gauge, stirrer and thermocouple was used as the reaction vessel. Pt/substrate ratio was 0.001 (molar) and CAL/isopropanol ratio was 0.03 (by wt.) for all the catalytic reactions. Catalysts were pre-activated at 100 °C for 2 h in 35 mL isopropanol under 34 bar hydrogen pressure (RT) before the reaction. 1.25 g of cinnamaldehyde in 40 mL of isopropanol was charged in the reactor and heated to 60 °C under a H<sub>2</sub> pressure of 30 bar at RT. At intervals, aliquots of the reaction mixture were taken from the reactor and GC analysis was performed on Agilent Technologies 6890N Network GC system using an HP5 column.



Fig. 1. Cinnamaldehyde hydrogenation on Pt/mSiO<sub>2</sub> catalysts with varying Pt particle sizes; top: conversion and product yield (%) vs. time, bottom: product selectivity vs. conversion for 1.8, 3.6, 4.9 and 8 nm (■ CA; ● HCAL; ▲ PP; ▼ CAL).

#### 3. Results and discussion

We have recently reported a novel in-situ method for encapsulation of Pt nanoparticles exclusively within the channels of mesoporous silica [12,13]. We have synthesised Pt nanoparticles of sizes 8 and 4.9 nm by employing two different polymer templates, P123 and Brij-76 modified with cationic surfactant CTAB for better metal precursor anchoring. The silica channels act as moulds during the formation of the nanoparticles and also prevent further agglomeration during reactions. We also synthesised two more catalysts with Pt particles of sizes 1.8 and 3.6 nm by encapsulating already formed nanoparticles in 2D hexagonal mesoporous silica following the procedures reported elsewhere [14]. In both of these types of catalysts, the particles are reasonably monodisperse and hence ideal for selective reactions dependent on particle sizes.

Selective cinnamaldehyde (CAL) hydrogenation was carried out on the above four catalysts and a kinetic analysis was done based on the results. In the given reaction conditions, three products i.e. cinnamyl alcohol (CA), hydrocinnamaldehyde (HCAL), and phenyl propanol (PP) are expected by hydrogenation of aldehyde, alkene and both aldehyde and alkene groups respectively [10]. Hydrogenation was effected by molecular hydrogen and transfer hydrogenation could be ruled out since no such product peaks could be identified. In the case of all the four catalysts, CA was obtained as the major product. Distribution of products of the reaction with time and variation of product yield/selectivity with conversion for all the catalysts are given in Fig. 1. After 1 h, 21% yield of CA is obtained at 40% conversion for Pt/mSiO<sub>2</sub>(1.8 nm). Yield increases with conversion up to a maximum of 52% after 10 h at 93% conversion. HCAL yield increases up to 18% at 5 h at 74% conversion after which it starts decreasing. Amount of PP increases as reaction proceeds and at the end of the reaction i.e. at 10 h, it reaches 27%. Similar trends were observed for the other three catalysts. PP amount is found to increase steadily at first and as the reaction proceeds, it seems to increase in tandem with a decrease in HCAL formation. This indicates that HCAL gets hydrogenated with time as its concentration increases to give PP. This points to a set of parallel and consecutive reactions. From these observations it is clear that the yield of CA increases with increase in particle size and follow the order 8 nm>4.9 nm>3.6 nm>1.8 nm. Since the support, i.e. 2D mesoporous silica, is the same for all the four catalysts this effect can be attributed solely to the particle size. It is noteworthy here that we could achieve very high selectivity of the order of 80% in Pt/mSiO<sub>2</sub>(8 nm) catalyst with low loading of Pt whereas in conventional catalysts higher loading is necessary for obtaining bigger nanoparticles. Selectivities of CA at 50% and 75% conversions on various catalysts are given in Table 1.

As clear from the table, Pt/mSiO<sub>2</sub> (1.8 nm) with the smallest particle size gives minimum selectivity while Pt/mSiO<sub>2</sub> (8 nm) with largest particle size gives maximum selectivity. Apparently, C=O bond is hydrogenated faster than C=C bond, yielding more CA. Although HCAL is also obtained as a result of hydrogenation of C=C bond initially, C=O bonds get further hydrogenated to give PP which is the final product. Increase in selectivity of CA from 57% to 80% as particle size increases from 1.8 nm to 8 nm can be attributed to change in the extent of exposure of different crystallographic planes with increasing particle size; [111] planes being more sterically hindering for C=C approach to the surface [15–17].

Table 1

Selectivity of cinnamyl alcohol at 50%  $(S^{50})$  and 75%  $(S^{75})$  conversions on various catalysts.

Catalyst	Av. Pt particle size (nm)	S <sup>60</sup>	S <sup>75</sup>
Pt/mSiO <sub>2</sub> (1.8 nm)	1.8	50	57
Pt/mSiO <sub>2</sub> (3.6 nm)	3.6	68	67
Pt/mSiO <sub>2</sub> (4.9 nm)	4.9	73	68
Pt/mSiO <sub>2</sub> (8 nm)	8	87	79

The above results and analysis of the graphs indicate that PP is predominantly formed from HCAL and not at the expense of CA. Hence the following scheme (Scheme 1) was considered for further kinetic analysis. This can be considered as a set of parallel reactions in which one of the steps (CAL to HCAL) is a series reaction which continues further to form PP. As hydrogen used is in excess, the set of reactions was considered as pseudo-first order reactions. Mass transfer effects were not considered since stirring rate was adjusted so that such effects were negligible. Moreover, adsorption was assumed to be the rate limiting step and the following pathways were adopted.

#### 3.1. Step-1 parallel reaction

At any time, the total concentration of HCAL formed consists of the concentrations of HCAL and PP. Hence, it is possible to take the total HCAL formed is equal to the moles of HCAL + moles of PP.

$$\begin{array}{l} C_{HCAL(Total)} = C_{HCAL} + C_{PP} \\ \hline Selectivity for HCAL, s &= HCAL(Total)/CA \\ &= (C_{HCAL} + C_{PP})/CCA \\ \end{array} \tag{1}$$

Here  $C_{HCAL}$ ,  $C_{PP}$  and  $C_{CA}$  are the concentrations in moles of hydrocinnamaldehyde, phenyl propanol and cinnamyl alcohol, respectively.

The rate of disappearance of CA, according to first order parallel reaction, can be written as,

$$-d(C_{CAL})/dt = k_1C_{CAL} + k_3C_{CAL} = (k_1 + k_3)C_{CAL}$$

which, on integration gives

$$\ln(1 - X_{CAL}) = (k_1 + k_3)t.$$
(2)

Here C<sub>CAL</sub> is the concentration of cinnamaldehyde, X<sub>CAL</sub>, its conversion and t, the reaction time.  $(k_1 + k_3)$  was obtained from the slope of the linear plot of  $-\ln(1 - X_{CAL})$  versus t, passing through the origin.  $k_1/k_3$  was calculated from the average selectivity (Eq. (1)) obtained from the experimental data. These values were used for determining  $k_1$  and  $k_3$ .

#### 3.2. Step-2 series reaction

The rate constant  $k_2$  of the series reaction (formation of PP from HCAL) was obtained from the standard equation for the concentration of the intermediate compound in a series reaction, which is given by

$$C_{\text{HCAL}} = C_{\text{CAL0}} k_1 \left( \frac{e^{-k_1 t}}{k_2 - k_1} - \frac{e^{-k_2 t}}{k_2 - k_1} \right)$$

or

$$\frac{CHCAL}{CCAL0\,k_1} = \frac{e^{-k_1t} - e^{-k_2t}}{k_2 - k_1}.$$
(3)



Scheme 1. Scheme for kinetic analysis of cinnamaldehyde hydrogenation.



Fig. 2. Variation in rate constants for the series and parallel steps with the particle size.

Eq. (3) was used for the estimation of  $k_2$  by trial and error method. The values of  $k_1$ ,  $k_2$  and  $k_3$  obtained for different catalyst sizes are given in the Supplementary material. Fig. 2. represents the variation in rate constants with particle size.

It reveals that the rate constant for the formation of PP is higher and more sensitive to the catalyst size than those of the other two products. However, the formation of PP is restricted by the formation of the intermediate HCAL. The rate constant for the formation of HCAL is the lowest and decreases with increase in particle size. Hence a higher concentration of CA in the product is obtained in the experiments even though formation of PP is the most favoured reaction kinetically. This indicates that adsorption through C=O is the most favoured geometry. However, HCAL formation being the most sluggish prevents higher yields of PP leading to selective hydrogenation to CA. Parity plots between the experimental concentrations and the predicted concentrations (CCAL/CCAL<sub>0</sub> vs. CCAL//CCAL<sub>0</sub>, CCHAL/CCAL<sub>0</sub> vs. CCAL//CCAL<sub>0</sub> vs. CCAL//CCAL<sub>0</sub> vs. CCAL//CCAL<sub>0</sub> vs. CCAL//CCAL<sub>0</sub> vs. CCAL//CCAL<sub>0</sub> and CCAL/CCAL<sub>0</sub> vs. CCAL//CCAL<sub>0</sub> are presented in Fig. 3. Only points in the linear increase region of the yield vs conversion graphs were used in these calculations. The figure shows that the points cluster around the Y = X trend line indicating that the prediction matches reasonably well with that of the experimental values, confirming the validity of the reaction path way.

#### 4. Conclusion

Pt particles of varying sizes are isolated within the channels of mesoporous silica compounds. Cinnamaldehyde hydrogenation showed sensitivity to Pt particle sizes and the selectivity to cinnamyl alcohol increased with increasing particle sizes. Cinnamyl alcohol was found to be the major product with hydrocinnamaldehyde further forming fully hydrogenated product phenyl propanol. A kinetic analysis based on a set of parallel and consecutive reaction pathways revealed that the rate of phenyl propanol formation is the highest and most sensitive to Pt particle size. As particle size increases, complete hydrogenation of hydrocinnamaldehyde is preferred; however, the sluggishness of



Fig. 3. Plots of experimental versus theoretical concentrations (molar ratio) for the hydrogenation of cinnamaldehyde over Pt-mSiO<sub>2</sub> catalysts with Pt nanoparticles of different sizes at 60 °C and 30 bar H<sub>2</sub> pressure.

hydrocinnamaldehyde formation leads to the enhanced yield of cinnamyl alcohol.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http:// dx.doi.org/10.1016/j.catcom.2012.08.017.

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