Shape Controlled Palladium Nano Particles for Hydrogenation of Cinnamaldehyde

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Abstract. Palladium nano particles in tetrahedral (Td), octahedral (Oh) and spherical (Sp) shapes, supported on hydrotalcite, were synthesized and characterized by XRD and TEM. Td shaped Pd nano particles, with maximum number of exposed (111) planes of Pd, display maximum turn over frequency (TOF) / intrinsic activity for hydrogenation of cinnamaldehyde, indicating the importance of active site geometry. Oh & Sp shaped Pd nano particles that expose both (111) and (100) planes have relatively lower intrinsic activity. For a given reaction, it is essential that appropriate active site geometry, as dictated by the shape/morphology of nano particles be made available. Synthesis and stabilization of such shape controlled nano particles is of prime importance in developing catalysts with higher activity.

Keywords: Pd nano particles, shape control, active site geometry, cinnamaldehyde, hydrogenation, TOF.

1 Introduction

Supported metal catalysts have been extensively studied, as they display high activity, selectivity, stability under mild reaction conditions as required in many catalytic reactions [1]. A number of factors are known to influence the performance of supported metal catalysts [2], namely, the metal loading, nature of metals, crystallite size, metal surface morphology, nature of the support, addition of second/promoter elements [3], the metal–support interactions and method of preparation [4]. Of these, the crystallite size and morphology of the metal particles are the two important factors affecting the number and nature/geometry of the active sites, which in turn influence activity and selectivity respectively. Nano size metal particles with different sizes and shapes have different degrees of dispersion, exposed facets and fractions of atoms located at different corners, edges, and defects, each having specific activity/selectivity. Thus, for a given reaction, the catalytic activity of particles with different morphology can vary significantly. Semagina and Kiwi-Minsker [5] compared the activity of nano size Pd hexagons and spheres for hydrogenation of 2-methyl-3-butyn-2-ol and observed that nano spheres with maximum amount of exposed (111) planes displayed highest TOF. Role of shaped Pd nano crystals in controlling activity & selectivity for various reactions by influencing the facets, and relative populations of atoms in edges, corners and planes has been reviewed in detail by Zhang et al [6]. Wang et al. [7] reported that silica supported Pd nano particles in octahedral shape (with predominantly (111) planes) was more active for CO oxidation compared to cubic Pd (with (100) facet) while the facet activity pattern was exactly reverse in the case of silica supported Pt. Hence, studies on the preparation, characterization and performance evaluation of shape controlled supported metal catalysts has been area of tremendous importance both from basic as well as applied aspects of catalysis. In the present work, we have explored the effect of Pd nano particles in tetrahedral (Td), octahedral (Oh) and spherical (Sp) shapes, supported on hydrotalcite (HT), using hydrogenation of cinnamaldehyde as the model reaction.

2 Experimental

2.1 Materials

Palladium chloride (Sisco Research Laboratories), poly vinyl pyrrolidone (PVP), ethylene glycol (EG), sodium hydroxide (NaOH), magnesium nitrate hexa hydrate ($Mg(NO_3)_2 \cdot 6H_2O$), aluminum nitrate

nonahydrate $(Al(NO_3)_3 \cdot 9H_2O)$, cetyl trimethyl ammonium bromide (CTAB) from Sigma Aldrich, hexamethylenetetramine (HMTA), cinnamaldehyde and methanol (Qualigens) were of analytical reagent (AR) grade and used as such.

2.2   Preparation of Shape Controlled Pd/Hydrotalcite (HT) Catalysts

Palladium supported on hydrotalcite catalysts were prepared by adopting precipitation-reduction method [8] wherein the precipitation of the hydrotalcite support and reduction of Pd ions from the respective metal precursor salts proceed simultaneously in presence of hexamethylenetetraamine (HMTA). Decomposition of HMTA under hydrothermal conditions liberates ammonia and formaldehyde. While the precipitation of the Mg-Al hydrotalcite is initiated by ammonia, formaldehyde effectively reduces Pd^{2+} to Pd^0.

1.0 % (w/w) Pd/HT in Tetrahedral (Td) Shape To an aqueous solution containing 3.01 g (11.7 mmol) of $Mg(NO_3)_2 \cdot 6H_2O$, 2.19 g (5.84 mmol) of $Al(NO_3)_3 \cdot 9H_2O$ and 5.76 g (41.0 mmol) HMTA in 45 ml of de-ionized water, another aqueous solution containing 0.0157 g (0.00884 mmol) of $PdCl_2$ and 0.01035 g (0.17 mmol) of NaCl in 5 ml of de-ionized water was added and mixed together and then transferred into an autoclave. The autoclave was heated to 150 °C for 6 h. Subsequent to natural cooling, the precipitate was filtered and washed with de-ionized water until the pH value of the filtrate reached 7 and finally dried overnight at 100 °C.

1.0 % (w/w) Pd/HT in Octahedral (Oh) Shape The procedure was similar to that adopted for tetrahedral shaped catalyst, except that in the first solution 1.3 g (3.56 mmol) of CTAB was added along with salts of Mg & Al and HMTA. After the addition of second solution, the mixture was subjected to similar autoclave treatment, cooled, filtered, washed and dried at 100 °C.

1.0 % (w/w) Pd/HT in spherical (Sp) Shape [9] Hydrotalcite support was prepared separately according to the method given above except adding Pd salt. A colloidal suspension of Pd nanoparticles was prepared separately by the reduction of $PdCl_2$ with ethylene glycol in alkaline medium in presence of PVP as the stabilizer. Initially H_2PdCl_4 was prepared by mixing 16.5 mg of $PdCl_2$ (0.059 mmol Pd) and 25 μ μL of concentrated HCl in a 100 mL glass beaker. A solution containing 25 mg of PVP (0.625 μ mol) and 6 mL of ethylene glycol was added followed by 0.75 mL of 0.31 M NaOH to H_2PdCl_4 solution. The mixture was stirred for ½ h at 60 °C to obtain a black colloidal suspension of Pd. To the Pd colloid, 0.99 g of hydrotalcite was added slowly and the temperature was increased to 110 °C using oil bath. The mixture was stirred continuously, monitored carefully till ethylene glycol was expelled. The catalyst was then dried in hot air oven overnight at 100 °C.

3.6 % (w/w) Pd/HT in Td, Oh & Sp Shapes The procedures were similar to those adopted for the three different shaped catalysts with 1.0 % (w/w) Pd loading, except that appropriate amounts of Pd salt precursors were used to achieve Pd loading of 3.6 % w/w.

2.3   Characterization of Catalysts

X-ray Diffraction (XRD) XRD pattern of the sample was recorded using Rigaku Miniflex (II) X-ray diffractometer using Cu Kα radiation source ($\lambda = 1.5401$ Å) with a scan rate of 3°/min, in the 2θ range of 5-90°.

Transmission Electron Microscopy (TEM) TE micrographs were recorded on JEOL 3010 model (200 kV). Few milligrams of the sample (1-2 mg) were dispersed in few mL (4-5 mL) of ethanol by ultra-sonication for 15 minutes and the sample was kept aside for 10 min. A drop of the top layer was placed on a carbon coated copper grid and allowed to dry in air at room temperature. ImageJ software was used to calculate the crystallite sizes. Based on the mean crystallite size measured from TEM data, Pd metal dispersion was calculated using the formula (1)[10].

$$\text{dispersion } (\%) = \frac{600 \cdot M_{Pd}}{\rho_{Pd} \cdot d_{nm} \cdot a_{Pd} \cdot N_a} \tag{1}$$

where, M_{Pd} is the molecular weight of Pd (106.4 g/mol), a_{Pd} is the atomic surface area of Pd (6.8×10^{-20} m^2/atom), ρ_{Pd} is the density of Pd (12.02 g/cm³), N_a is Avogadro's number, and d_{nm} is the average crystallite diameter (in nm) estimated from TEM data. Dispersion and the rate of hydrogenation of cinnamaldehyde (r) were used to calculate the turnover frequency, according to the formula (2)[10].

$$\text{TOF}(\text{s}^{-1}) = \frac{r}{n_{tot} \cdot \text{dispersion}(\%)} \qquad (2)$$

Where r is the rate of hydrogenation (moles converted per second), n_{tot} is the total number of Pd moles in the reactor.

2.4   Hydrogenation of Cinnamaldehyde

Catalysts were evaluated for liquid phase hydrogenation of cinnamaldehyde (CAL) in a 100 mL Parr reactor (Model 4848) with methanol as the solvent. Reactions were conducted at 100 °C, with 40 mg of catalyst dispersed in a reaction medium containing a mixture of 13 g of methanol and 2.4 g of CAL was adopted as the standard reaction condition and hence applied to all catalysts. Prior to reaction, the reactor was first purged three times with nitrogen, followed by purging three times with H_2 gas and then pressurized to 10 bar. The reaction was carried out for 1 h after the desired reaction temperature was reached. After each reaction, the reactor was allowed to be cooled naturally to room temperature and depressurized. The catalyst and reaction products were separated by filtration and the product stream was analyzed in PerkinElmer Clarus-500 GC equipped with FID and RTX-5MS capillary column. Hydrocinnamaldehyde (HCAL), cinnamyl alcohol (COL) and hydrocinnamyl alcohol (HCOL) were identified as the products. Since methanol was used as solvent, some amount of acetal formation was observed along with hydrogenation products. After accounting for the formation of acetal, the amount of CAL involved in hydrogenation reaction was estimated and conversion of CAL to hydrogenation products and TOF for hydrogenation was then calculated accordingly.

3   Results and Discussions

3.1   Characterization of Catalysts

X-ray diffraction patterns for 3.6 % w/w Pd/HT catalysts (Fig.1) have been considered for characterization studies since d-line due to Pd (111) planes in 1% (w/w) Pd/HT samples could not be observed clearly, because of interference by the d-line for (015) planes of HT phase. With Pd content at 3.6 % (w/w) d-line due to Pd (111) planes at 2θ=40.01° could be clearly seen (Fig.1 inset) for Td, Oh & Sp shaped catalysts along with high intensity d-lines at low angles corresponding to (003) & (006) planes of hydrotalcite phase. Intensity of (111) line is more prominent for Td shaped Pd than that for Oh & Sp shaped Pd, since the Td phase exposes only (111) planes while Oh & Sp phases expose both (111) as well as (100) planes [8].

Transmission electron micrographs for 1% Pd (w/w)/HT catalysts that exhibit different morphology are given below (Fig.2), along with respective histograms. The mean crystallite sizes measured are: 26.03 nm (Td shaped), 25.73 nm (Oh shaped) and 3.63 nm (Sp shaped). Crystallite size values obtained for Td and Oh shaped catalysts are close to those reported by Feng et al [8] whose method of preparation has been adopted in the present work. While the thermodynamically favoured morphology under high Pd^{2+} reduction rates is cubooctahedral (Spherical). With slow decomposition of HMTA to form formaldehyde as reductant, the reduction rate is slow. Hence, nano particles with tetrahedral morphology are formed during simultaneous precipitation of HT and reduction of Pd^{2+}. However, with CTAB as capping agent, Br^- ions bind preferentially to Pd (100) than to Pd (111), hence growth of (100) facets is enhanced and truncated octahedron shape with both (111) and (100) facets being observed [8]. Since the spherical shaped 1% Pd (w/w)/HT catalyst was prepared by a different method [9], the mean Pd crystallite size is smaller at 3.63 nm, with its surface enclosed by mixture of facets (111) and (100) [11].
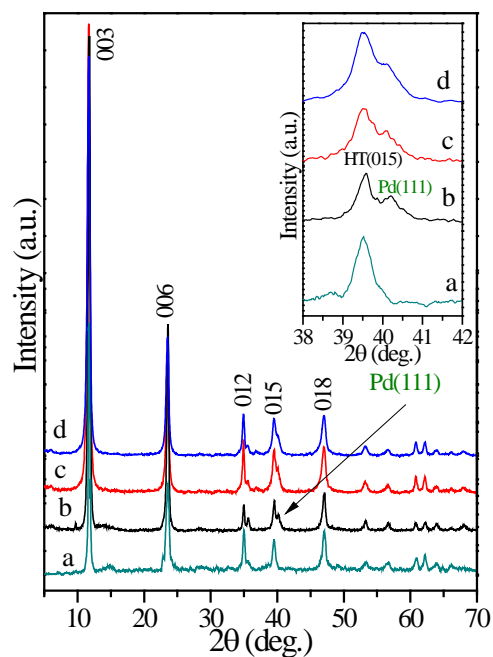
Figure 1. XRD patterns for 3.6 % (w/w) Pd/HT catalysts: a) Hydrotalcite b) Tetrahedral c) Octahedral d) Spherical.
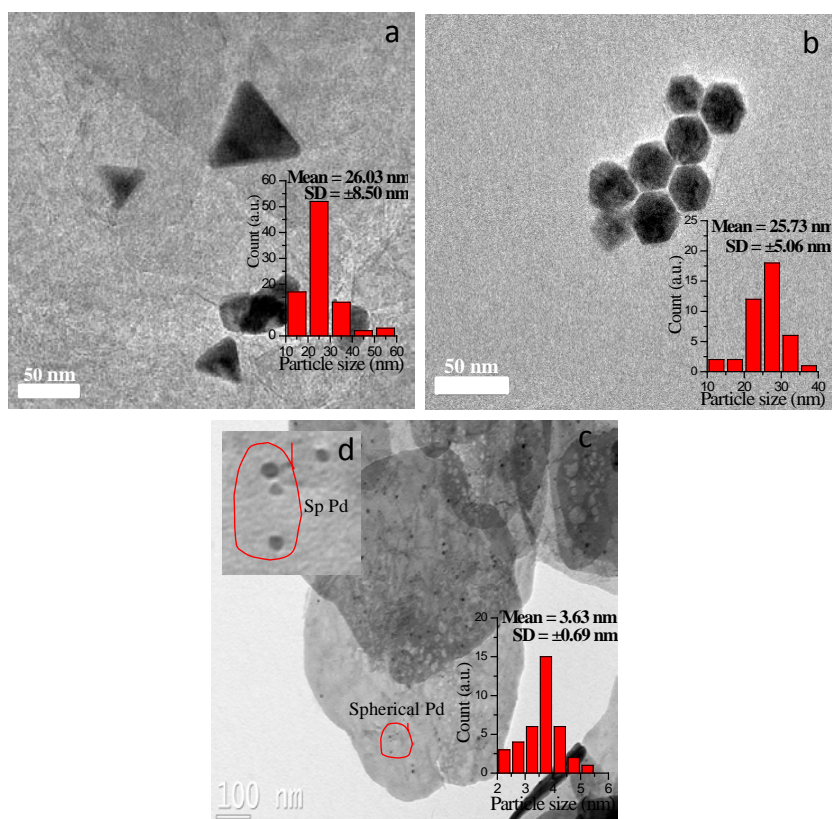

Figure 2. TE micrographs and histograms for a) Tetrahedral b) Octahedral and c) Spherical shaped Pd nano particles supported on hydrotalcite with inset d showing magnified view of Sp Pd nanoparticles.

3.2 Influence of Shape of Pd Nano Particles

Based on the particle size values, Pd metal dispersion values were calculated using the formula (1). Dispersion values and CAL hydrogenation rate data were then used to calculate the turn-over frequency (TOF) values for the three catalysts according to formula (2). TOF values presented in Table.1 clearly show that Td shaped catalyst is more active than Oh and Sp shaped catalysts. Td shaped Pd nano particles with maximum number of exposed (111) planes, having maximum density of Pd atoms, display maximum TOF amongst the three catalysts. As Oh & Sp shaped Pd nano particles expose both (111) and (100) planes, overall activity is less. Though the crystallite size of spherical Pd particles is small, hence the number of active sites is higher, the intrinsic activity (activity per site per unit time) is less, as the requisite active site geometry is not available. Thus, besides the crystallite size/dispersion, the shape/morphology of nano particles, that determine the active site geometry, is crucial for higher activity. Similar concept was proposed by Semagina and Kiwi-Minsker [5] who observed that the activity of nano size Pd hexagons for hydrogenation of 2-methyl-3-butyn-2-ol is less vis-à-vis nano spheres with maximum amount of exposed (111) planes. Zheng et al. [12] have demonstrated that for electro oxidation of formic acid, Pd nano cubes with exposed (100) planes are more active than Pd nano spheres of same size, due to favourable mode of adsorption of formic acid on (100) planes. It is therefore amply clear that for a specific reaction pathway, it is essential that appropriate active site geometry, as dictated by the shape/morphology of metal nano particles be made available. Invariably, synthesis and stabilization of such shape controlled nano particles is achieved by adopting suitable preparation methods.

Table 1. Activity and selectivity data for hydrogenation of cinnamaldehyde on 1% Pd (w/w)/HT Catalysts: Influence of the shape of Pd nano particles

Shape	Conv. (%)	Selectivity of products (%)			TOF x10^{-2} (Sec^{-1})
		HCAL[1]	HCOL[2]	COL[3]	
Tetrahedral	25.7	94.2	0.0	5.7	7.3
Octahedral	13.9	98.0	1.9	0	3.7
Spherical	62.3	84.9	3.6	11.4	2.3

Conditions: Temp.100 °C; Cat. wt. - 40 mg; 13 g methanol; 2.4 g CAL[4]; 10 bar H$_2$; Reaction time -1 h
[1]Hydrocinnamaldehyde; [2]Hydrociinnamyl alcohol; [3]Ciinnamyl alcohol; [4]Cinnamaldehyde
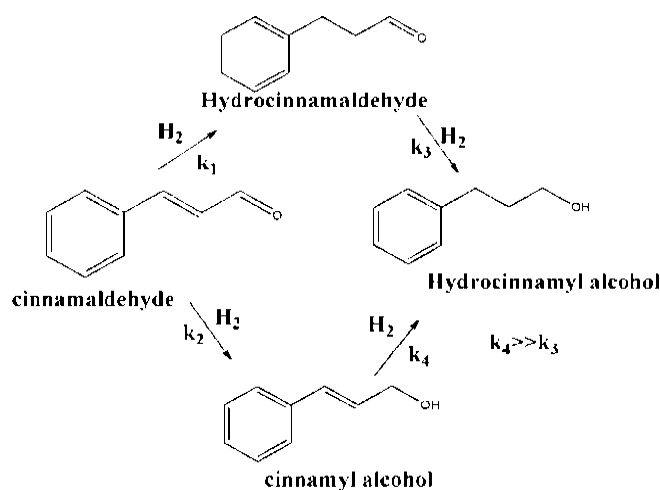
Scheme 1. Reaction pathways for hydrogenation of cinnamaldehyde.

Interestingly, both Td & Oh shaped Pd display very low selectivity for COL vs. ~11 % by spherical particles, indicating that mode of adsorption of CAL (through C=C or C=O bond) could perhaps dictate the selectivity towards COL. Further investigations are needed on this issue. Besides, the major product is HCAL with very low selectivity for HCOL, implying that the rate of conversion/further

hydrogenation of HCAL to HCOL is very slow as depicted in the Scheme 1 above for hydrogenation of CAL.

4   Conclusions

Pd nano particles (1% w/w) in different shapes, i.e., tetrahedral, octahedral and spherical, supported on hydrotalcite, were prepared by simultaneous formation of hydrotalcite phase and palladium nano particles from the respective precursor salts and characterized by XRD and TEM studies. Tetrahedral shaped particles with maximum exposure of (111) planes display maximum TOF/intrinsic activity for hydrogenation of cinnamaldehyde. Octahedral and spherical shaped catalysts with the exposure of (111) and (100) planes display lower activity. Controlling morphology/shape of nano particles is crucial in order to expose appropriate crystal planes/active phase geometry suitable for the desired reaction pathway.

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