A water soluble nanostructured platinum (0) metal catalyst from platinum carbonyl molecular clusters: Synthesis, characterization and application in the selective hydrogenations of olefins, ketones and aldehydes

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Abstract

High nuclearity platinum carbonyl cluster anions (Chini's clusters) have been used as precursors to prepare a platinum nanocatalyst. The ionic polyelectrolyte poly(diallyldimethylammonium chloride) has been used as the support material for anchoring $[Pt_{30}(CO)_{60}]^{2-}$ via ion-pairing and subsequent stabilization of the nanoparticles. The polymer-supported material has been studied by spectroscopy (NIR, ^{13}C NMR, and IR) and TEM before and after its use as a water soluble hydrogenation catalyst. The nanocatalyst is found to be effective for the chemoselective hydrogenation of olefinic, aldehydic and ketonic double bonds. For most of the substrates isolation of the product and reuse of the catalyst are extremely easy due to the automatic phase separation of the products from the catalyst. The spectral features of the fresh catalyst show retention of the carbonyl ligands and molecular identity of the parent cluster, but after use the carbonyl ligands appear to be lost. TEM of the supported material before and after use as a catalyst shows the presence of platinum nanoparticles with majority ($\geq 70\%$) of the particles in the range of 2–6 nm. Smaller particles are dominant in the used catalyst and this observation is rationalized on the basis of the known reactivity of Chini's clusters with dihydrogen.

Keywords: Platinum carbonyl cluster; Hydrogenation catalysts; Water soluble polymer; Nanocatalyst

1. Introduction

The use of water rather than volatile organic solvents is an important theme of current chemical research [1–5]. Apart from the obvious environmental friendliness and safety, easy separation of water immiscible or insoluble organic product is an added attraction of water based industrial processes [6,7]. Catalysis by metal colloids and/or nanoparticles is another emerging area of considerable promise [8–10]. High selectivity and recyclibility have been reported for a variety of nanocatalyst-based organic reactions [8–10]. There is a recent report where selectivity of the nanocatalysts has been found to be critically dependent on the solvents employed [11]. While major effort has been made to recycle nanocatalysts using dendrimers, solid support, etc., the use of *ionic polyelectrolytes* for such a purpose remains virtually unexplored.

The advantages of water as a reaction medium and nanoparticles as catalysts prompted us to investigate platinum nanoparticles catalyzed hydrogenation reactions in water. We report here that ion pairing of high nuclearity platinum carbonyl clusters on water soluble poly(diallyldimethylammonium chloride), **1**, leads to the facile formation of CO-protected platinum nanoclusters. This material, **2** (see Scheme 1) is a precursor to a water soluble catalyst that selectively catalyzes the hydrogenation of olefinic, aldehydic, and ketonic unstaurations. Spectral data and TEM micrographs of used **2** indicate that during hydrogenation the carbonyl ligands are lost, but the platinum particles do not undergo agglomeration, and in fact, they retain their nanometric features.
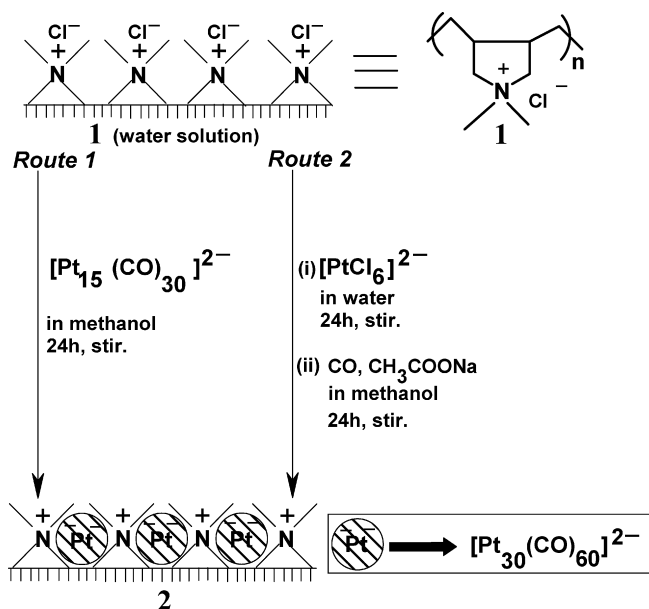
Scheme 1. Formulation of catalyst.

2. Experimental

2.1. Materials and methods

Preparation of the nanoclustered materials and their subsequent manipulation were performed using standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures (methanol over Mg-turnings/iodine), distilled under nitrogen, and used immediately. Poly(diallyldimethylammoniumchloride) (poly-DADMAC, low mol. wt.), 20 wt.% solution in water, sodium hexachloroplatinate, methyl pyruvate, acrylic acid and styrene were purchased from Aldrich, Germany. Absolute ethanol, carbon tetrachloride, iodine, mercuric chloride, potassium iodide and sodium thiosulphate were purchased from Sd fine chemicals, Mumbai. All other chemicals were of reagent grade and used after proper distillation prior to the catalytic experiments. Distilled water was used for the catalytic studies in water or a water biphasic medium. $Na_2[Pt_{30}(CO)_{60}]$ and $Na_2[Pt_{15}(CO)_{30}]$ were synthesized according to the procedures reported in the literature [12]. All the hydrogenation reactions were carried out in an autoclave. Conversions in the hydrogenation reactions with different substrates were monitored by a Shimadzu GC-14A gas chromatograph technique with an FID detector using a capillary column (CBP20-M-25-025, Shimadzu capillary column, length 25 m, inner diameter 0.25 mm, film 0.20 mm). All hydrogenated products were initially identified by using authentic commercial samples of the expected products. The extent of hydrogenation of safflower oil and acrylic acid were measured by ^{1}H NMR. Thermo Nicolet 320 FT-IR and Perkin Elmer Lambda 950 UV–Vis–NIR spectrophotometers were used for recording IR and UV–Vis–NIR spectra, respectively. ^{1}H/^{13}C NMR spectra were recorded on a 400 MHz Varian spectrometer. TEM experiments were performed using a Philips 1200 EX at 120 kV. The bulk platinum content of fresh catalyst **2** was determined on an 8440 Plasma Lab ICP-AES instrument.

2.2. Synthesis of catalyst 2

Catalyst **2** has been prepared in two different ways.

(a) Low molecular weight polydiallyldimethylammoniumchloride (Aldrich, Average $M_w = 100,000$–$200,000$, 20 wt.% water solution, 3 mL) was added drop-wise to a methanolic solution of $[Pt_{15}(CO)_{30}]^{2-}$. $[Pt_{15}(CO)_{30}]^{2-}$ was prepared according to the procedure reported in the literature [12] from Na_2PtCl_6 (100 mg). Upon continuous stirring for 48 h, the color of the solution changed from deep green to brown-black. The solution was then reduced to minimum volume under reduced pressure. On storage, a brown-black mass separated out, which was washed with small amount of cold methanol followed by acetone and dried under vacuum.

(b) Alternatively, a solution of Na_2PtCl_6 (100 mg in 5 mL water) was added drop-wise to the low molecular weight polymer solution (20 wt.% water solution, 3 mL) under constant stirring for 24 h. The solution was then reduced to minimum volume under reduced pressure. On storage an orange solid separated out which was dissolved in methanol (15 mL) and sodium acetate (124 mg) was added. On stirring under a CO atmosphere for 12 h the solution turned greenish brown. On removal of solvent under reduced pressure, brown-black solid (**2**) was obtained. Samples prepared by these procedures exhibit identical spectral features (see Section 3.1). The bulk platinum content in **2** prepared by both the methods has been found to be $\sim1.0 \pm 0.05\%$ from ICP-AES analysis of an aqueous solution of **2**.

2.3. Catalytic experimental conditions

All hydrogenation reactions were carried out in an autoclave under hydrogen (50 bar) pressure at 300 K unless otherwise specified. In a typical experiment 150 mg of catalyst was dissolved in 10 mL distilled water in a 20 mL beaker and 1 g of substrate was added to it. Then the resulting mixture was kept under 50 bar hydrogen pressure in the autoclave at 300 K for a specified time with vigorous stirring. After the reaction, the product was recovered by means of decantation and/or solvent extraction and subsequently analyzed by GC and NMR spectroscopic techniques.

3. Results and discussion

3.1. Synthesis and characterization of the nanocatalyst before its use in a catalytic run

Several methods have been reported in the literature for the synthesis of platinum nanocatalysts [13–22]. We have shown recently that Chini's clusters, $[Pt_{15}(CO)_{30}]^{2-}$ and $[Pt_{12}(CO)_{24}]^{2-}$, can be ion-paired with quaternary ammonium groups of functionalized inorganic materials such as MCM-41 and fumed silica as well as organic polymers [23–26]. It has

also been shown that platinum colloids can be carbonylated [27] to give $[Pt_{15}(CO)_{30}]^{2-}$. As **1** is water soluble, and NR_4^+ ions are known to stabilize metal nanoparticles, [9] we reasoned that ion pairing of Chini's clusters with the quaternary nitrogen atoms of **1** might provide the precursor to a water soluble, high performance nanostructured catalyst.

Addition of an aqueous solution of **1** to a methanolic solution of $[Pt_{15}(CO)_{30}]^{2-}$ leads to a color change from green to brown, and on removal of the solvent a dark brown material can be isolated. This material, **2**, is soluble in water and methanol, but is insoluble in all other common organic solvents. **2** can also be obtained by the reductive carbonylation of $[PtCl_6]^{2-}$ anchored onto **1** (see Section 2). The formulation of **2** *before it is used a catalyst*, as $[Pt_{30}(CO)_{60}]^{2-}$ ion-paired on **1** (Scheme 1) comes from the following spectroscopic evidences.

Chini's clusters $[Pt_3(CO)_6]_n^{2-}$ ($n = 3–6$) have characteristic strong absorption bands in the visible region (500–850 nm). As reported and discussed by us in our earlier publications, these bands are conveniently used to identify the clusters and to monitor their reactions [28,29]. The synthesis of $[Pt_{30}(CO)_{60}]^{2-}$, Chini's cluster with highest nuclearity, was reported long time ago [12], but its electronic spectrum was never reported. This is because unlike $[Pt_3(CO)_6]_n^{2-}$ ($n = 3–6$), this cluster has no bands in the visible region. However, a near IR (NIR) spectrum of $[Pt_{30}(CO)_{60}]^{2-}$ shows that it does have a characteristic absorption at 1460 nm. As shown in Fig. 1a, the same band is also observed for **2** prepared either by the reductive carbonylation of $[PtCl_6]^{2-}$, or by the treatment of **1** with $[Pt_{15}(CO)_{30}]^{2-}$.
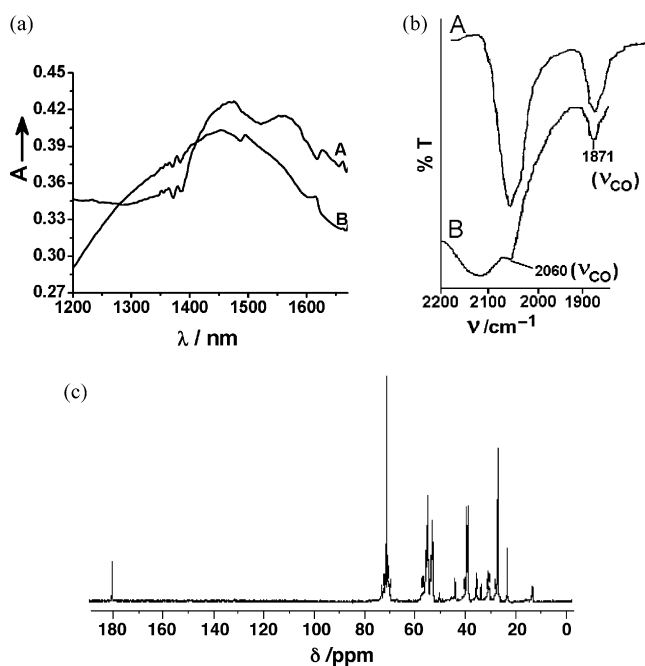

Fig. 1. (a) NIR spectra of $Na_2[Pt_{30}(CO)_{60}]$ and **2** in acetonitrile (A) and methanol (B), respectively, before using **2** as a catalyst. (b) IR(KBr) spectra of $Na_2[Pt_{30}(CO)_{60}]$ (A) and **2** (B) before its use as a catalyst. The band in (B) (br, vs) near 2100 cm^{-1} is due to the polymer, the inorganic carbonyls are at 2060 cm^{-1} (ν_{CO} terminal) and 1870 cm^{-1} (ν_{CO} doubly bridging). (c) ^{13}C NMR spectrum of **2** in D_2O. The peak at 180 ppm is due to inorganic carbonyl, the others from the polymer.
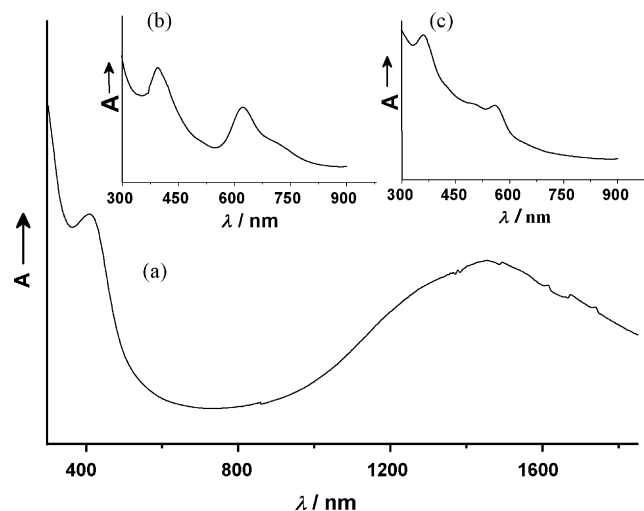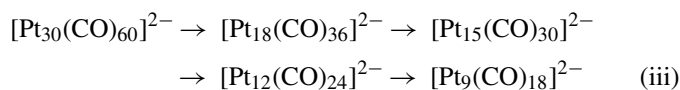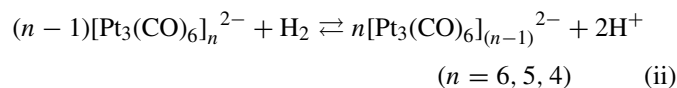

Fig. 2. (a) UV–Vis–NIR spectrum of a methanolic solution of freshly prepared **2**. (b) UV–Vis spectrum of methanolic solution of **2** after dihydrogen purging for 5 min, i.e. conversion of $[Pt_{30}(CO)_{60}]^{2-}$ to a mixture of $[Pt_{12}(CO)_{24}]^{2-}$ and $[Pt_{15}(CO)_{30}]^{2-}$. (c) UV–Vis spectrum of methanolic solution of **2** after prolonged (~30 min) dihydrogen purging; i.e. $[Pt_{30}(CO)_{60}]^{2-}$ fully converted to $[Pt_9(CO)_{18}]^{2-}$.

In the latter case, the change in nuclearity is caused by the well established redox chemistry of the Chini's clusters with protons (see below), i.e., reaction (i).
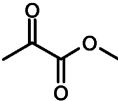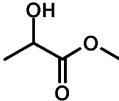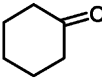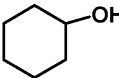
$$2[Pt_{15}(CO)_{30}]^{2-} + 2H^+ \rightarrow [Pt_{30}(CO)_{60}]^{2-} + H_2 \qquad (i)$$
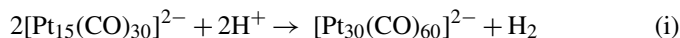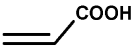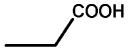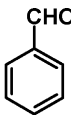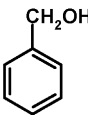
IR (KBr disk) spectra of $[Pt_{30}(CO)_{60}]^{2-}$ and **2** also show ν_{CO} bands at the same positions, 1870 and 2060 cm^{-1} (Fig. 1b). A D_2O solution of **2** in ^{13}C NMR shows a signal at 180 ppm (Fig. 1c) indicating that the cluster retains the CO ligands. Further evidence for the formulation of **2** comes from its reaction with dihydrogen. As shown in Fig. 2, on passing hydrogen through a methanolic solution of **2**, distinct spectral changes are observed. As mentioned earlier, the reactions of Chini's clusters with dihydrogen, which proceed according to (ii), have been thoroughly studied [28,29]. The observed spectrophotometric changes indicate that as shown by (iii), on reaction with 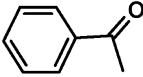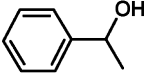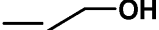dihydrogen, polymer supported $[Pt_{30}(CO)_{60}]^{2-}$ is converted to polymer supported $[Pt_9(CO)_{18}]^{2-}$ in a sequential manner.

$$(n - 1)[Pt_3(CO)_6]_n^{2-} + H_2 \rightleftarrows n[Pt_3(CO)_6]_{(n-1)}^{2-} + 2H^+$$
$$(n = 6, 5, 4) \qquad (ii)$$

$$[Pt_{30}(CO)_{60}]^{2-} \rightarrow [Pt_{18}(CO)_{36}]^{2-} \rightarrow [Pt_{15}(CO)_{30}]^{2-}$$
$$\rightarrow [Pt_{12}(CO)_{24}]^{2-} \rightarrow [Pt_9(CO)_{18}]^{2-} \qquad (iii)$$

3.2. Catalytic hydrogenation of olefinic, aldehydic and ketonic functionalities

Freshly prepared **2** has been used as a catalyst in water, for the hydrogenation of several representative substrates having >C=C or >C=O functionalities (see Table 1). As can be seen from the data given in Table 1, for most substrates full conversions and/or good turnover numbers (TON) could be obtained at ambient

Table 1
Catalytic performance of **2** for the hydrogenation of keto, aldehydic and olefinic substrates in water

Entry	Substrate	Product	Substrate amount (mmol), Time	%Conversion	TON[a]
1			2 g (19.59 mmol), 12 h	61	1466
2			1 g (10.18 mmol), 6 h	95	1185
3			2 g (27.54 mmol), 24 h	100	3404
4			1 g (9.60 mmol), 12 h	100	1179
5			1 g (10.62 mmol), 6 h	99	1145
6			1 g (8.32 mmol), 12 h	50	508
7			1 g (17.21 mmol), 12 h	100	2100
8	Safflower oil	Saturated fat	2 g (2.27 mmol), 24 h at 353 K	100	142

[a] TON = mmol of product/mmol of platinum. All the catalytic runs were carried out with 150 mg of **2** (8.15×10^{-3} mmol platinum) in 10 mL water under a hydrogen pressure of 50 bar with stirring. The reaction temperature was 80 °C for safflower oil and 27 °C for all the others.

temperatures. The only exception is safflower oil, which consists mainly (>80%) of the triglyceride of linoleic acid (*cis*, *cis* 9,12-octadecadienoic acid), where full conversion can be achieved at 80 °C. It may be noted that unlike the other substrates where the maximum number of carbon atoms is less than eight, safflower oil has 57 carbon atoms. The steric bulk of safflower oil may be partly responsible for the observed lower reactivity.

The hydrogenations of the $>$C$=$C (entries 3, 4, 7 and 8) and $>$C$=$O (entries 1, 2, 5 and 6) groups are totally chemoselective. Hydrogenations of the aromatic rings (entries 4, 5, and 6), acid functionality (entry 3) or the ester functionality (entries 1 and 8) are never observed. Ring hydrogenations with ruthenium molecular cluster catalysts in water were reported a few years ago, but have recently been shown to be caused by ruthenium metal formed from the molecular cluster [30,31]. In view of these reports, the absence of ring hydrogenation with **2** as the precatalyst is noteworthy. In reactions, where the products are alcohols (entries 1, 2, 5, 6, and 7), hydrogenolysis of the alcohol functionality is not observed either.

An obvious advantage of using **2** as a catalyst in water is the ease with which the catalyst could be separated from the product and reused. It may be noted that apart from acrylic acid and allyl alcohol (entries 3 and 7), all the other substrates are immiscible with water. Among the products, methyl lactate, propionic acid and propyl alcohol (entries 1, 3, and 7, respectively) are miscible with water. These products are separated from the water solution of the catalyst by solvent extraction. All the other products due

to their immiscibility with water could be very easily phase-separated and the catalyst was reused. This has been confirmed for the hydrogenation of styrene by recycling the catalyst three times without any noticeable change in its activities. In the case of safflower oil hydrogenation, the saturated fat separates out as a waxy solid.

3.3. TEM studies and fate of the nanocatalyst after its use in a catalytic run

TEM micrograph of freshly prepared **2** shows nanoparticles of platinum, with majority (∼75%) of the particles in the range of 2–6 nm (Fig. 3). The variation in size indicates loose aggregate formations by $[Pt_{30}(CO)_{60}]^{2-}$. By means of kinetic and ^{252}Cf-plasma desorption mass-spectrometric studies such aggregate formation with the Chini's clusters was shown to be a facile process [32]. The variation in the sizes of the nanoparticles in freshly prepared **2** is therefore an indication of the formation of loose aggregates of $[Pt_{30}(CO)_{60}]^{2-}$.

At the end of a catalytic run the IR spectrum of **2** does not show any inorganic carbonyl groups. The NIR band at 1460 nm also disappears. This indicates that $[Pt_{30}(CO)_{60}]^{2-}$ and its aggregates lose the CO ligands during the catalytic runs. TEM micrographs of used **2** show interesting differences from that of the freshly prepared **2**. As shown in Fig. 3, in comparison to the fresh catalyst there is an overall clear decrease in the size of metal nanoclusters in the used catalyst. Thus, in the fresh and
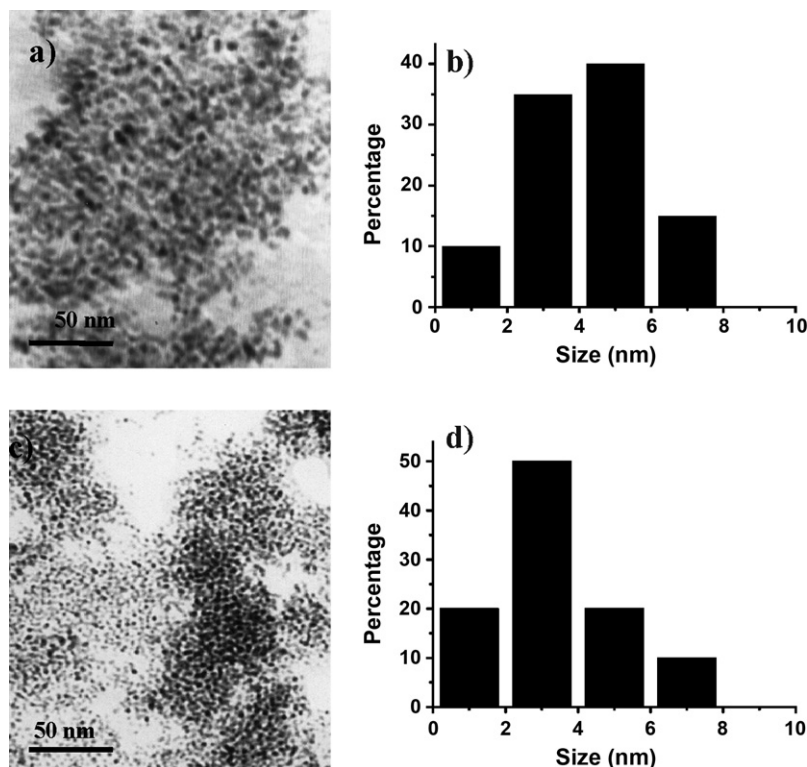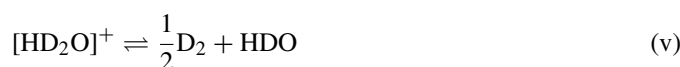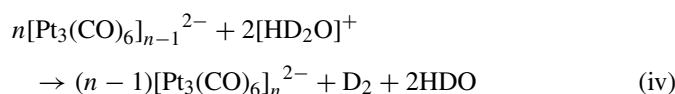
Fig. 3. (a and c) TEM images of freshly prepared and used **2**. (b and d) Number of particles (50 samples) against particle size of freshly prepared and used **2**.

used catalysts the number of particles in the range of 4–6 nm are ~40 and 20% while that within the range of 2–4 nm are 35 and 50%, respectively. A plausible explanation for smaller particles in used **2** lies in its known reactions with dihydrogen, i.e., reaction (iii), and the tendency to form aggregates. Under hydrogen pressure some of the $[Pt_{30}(CO)_{60}]^{2-}$ ions must be first converted to *lower nuclearity* clusters which then form aggregates and undergo decarbonylation. The overall decrease in size of the nanoparticles is therefore probably a reflection of the smaller size of the cluster units that undergo aggregation.

Further support for reaction (i) before decarbonylation sets in stems from comparative rate studies in water and D_2O. The *initial* isotope effect for the hydrogenation of styrene based on conversion over 20 min is >2, but over 50–60 min it is about 1.2. As shown by the stoichiometry of (ii), there exists a pathway for the equilibration between small amounts of H_2, HD and D_2 through the intermediacy of protonated D_2O. The protonated D_2O, i.e., $[HD_2O]^+$, can react with the lower nuclearity clusters according to (iv) which is the reverse reaction of equilibrium (ii). Thus, in the presence of the carbonylated platinum clusters, as shown by (v), $[HD_2O]^+$ will be in equilibrium with D_2 and HDO.

$$n[Pt_3(CO)_6]_{n-1}{}^{2-} + 2[HD_2O]^+$$
$$\rightarrow (n-1)[Pt_3(CO)_6]_n{}^{2-} + D_2 + 2HDO \qquad \text{(iv)}$$

$$[HD_2O]^+ \rightleftharpoons \frac{1}{2}D_2 + HDO \qquad \text{(v)}$$

However, this pathway is available *only during the initial* part ($\leq$20 min) of the catalytic run when the clusters retain the car-

bonyl groups. The amount of D_2 generated during this period is much smaller than the available H_2, and will be consumed quickly as the hydrogenation proceeds. The relatively large isotope effect observed only initially may therefore be indicative of Pt–H(D) bond formation or cleavage in the rate-determining step and is expected to be observed as long as there is D_2. Once most of the D_2 has been consumed, small secondary solvent isotope effect is observed.

4. Conclusions

In conclusion, ion pairing of Chini's clusters with the quaternary ammonium groups of **1** is found to be an effective method for the preparation of a nanostructured Pt(0) catalyst. Chemoselective hydrogenation of olefins, ketones and aldehydes are catalyzed in water by this catalyst. Spectroscopic and TEM studies of fresh and used catalysts indicate that the carbonyl groups are lost and that the particle size decreases during hydrogenation.

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