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Platinum Carbonyl Cluster Derived Catalyst of Superior Activity in Ketone and Unusual Selectivity in Nitrile Hydrogenation Reactions

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Summary: Hydrogenation catalysts have been prepared by ion pairing anionic platinum carbonyl clusters with quaternary ammonium groups on the surface of functionalized fumed silica and also by conventional adsorption methods. The catalytic performances of these materials have been compared with that of a commercial platinum catalyst in ketone and nitrile hydrogenation reactions. For ketone hydrogenation the catalyst made by ion pairing shows the best activity, while in nitrile hydrogenation both cluster-derived catalysts exhibit unusual chemoselectivity.

Carbonyl clusters supported on inorganic oxides have the potential to generate small metal crystallites with potentially novel catalytic properties and have been intensely studied for the last two decades.[1,2] While considerable progress has been made in elucidating structural details of cluster-derived particles, the practical advantages of such an approach for catalyst making remain to be firmly established. Studies that clearly show the superior performance of specially prepared cluster-derived catalysts, as compared to that of commercial catalysts, in important organic reactions are few. We report here the comparative performances of three platinum-based catalysts. Two of these, **1** and **2**, are carbonyl cluster derived, and the other one, **3**, is commercially obtained 5% Pt on alumina. We find that both the cluster-derived catalysts **1** and **2** (Scheme 1) are more active than the commercially purchased platinum catalyst **3** in ketone hydrogenation reactions. More importantly between **1** and **2**, the former is about 3 times more active than the latter. In the hydrogenation of nitriles the chemoselectivity of **1** and **2** on one hand and **3** on the other are also found to be very different.

The catalytic and other properties of the Chini clusters, $[Pt_3(CO)_6]_n^{2-}$ ($n = 3, 4, 5$), have been much studied.[2f,3a−h] We had reported the use of anion-exchange resin as a support material for a number of anionic carbonyl clusters, including the Chini clusters.[3e−g] The Chini clusters are especially attractive from the point of view of comparative performance studies between a commercially available and widely used platinum-based hydrogenation catalyst and a specially prepared cluster-derived catalyst. In the work presented here, as shown in Scheme 1, the Chini cluster $[Pt_{12}(CO)_{24}]^{2-}$ (**4**) is ion-paired on fumed silica, functionalized with tetra-alkylammonium groups, to give **1**. Catalyst **2** is prepared by the conventional adsorption of the sodium salt of **4** on fumed silica, while **3** is a commercially purchased platinum (5%) on alumina catalyst.[4] The purpose of comparing the catalytic activi-

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(4) In a typical synthesis of **1**, fumed silica (1 g, Aldrich) preheated under vacuum at 200 °C for 24 h was heated with 15 mL of $(OMe)_3Si(CH_2)_3Cl$ at 160 °C for 96 h. The Si^{29} NMR (MAS, Varian 300 MHz) spectrum of the resultant material isolated by filtration matches well with literature reported data (Sudholter, E. J. R; Huis, R.; Hays, G. R.; Alma, N. C. M. *J. Colloid Interface Sci.* **1985**, *103*, 554). The chloropropylsilane-functionalized fumed silica (1 g) was mixed with 10 mL of triethylamine and 5 mL of toluene. The mixture was heated at reflux for 96 h. It was then filtered and washed with toluene followed by methanol. The functionalized support (1 g) was treated with $Na_2[Pt_{12}(CO)_{24}]$ (0.2 g) in methanol (15 mL) at 25 °C for 96 h under CO atmosphere and was filtered under an atmosphere of CO. Freshly prepared **1** has IR signals (Nicolet Impact 400) and UV−vis (Shimadzu 165) bands that match well with that of $[Pt_{12}(CO)_{24}]^{2-}$ (ν_{CO} ~2060 and 1860 cm^{-1}, UV−vis band at ~620 nm). **1**: C, 18.4; H, 3.4; N, 0.7, Pt, 2.8 ±0.01 (Carlo Erba- 1106 C, H, N analyzer; GBC 902 double beam AAS). Surface platinum by EDAX (on several particles and at several locations after normalizing the average of each particle as one) from 0.82 to 1.31. Surface area 180 m^2/g, porosity 53%; pores are within 20−70 Å (BET analyzer). TEM (Philips CM 200) shows nanotubes of ~200 nm diameter with regular surface morphology. **2**: Fumed silica (1 g) was treated with $Na_2[Pt_{12}(CO)_{24}]$ (0.2 g) in methanol (15 mL) at 25 °C for 12 h under an atmosphere of CO. The slurry was taken to dryness under reduced pressure and washed once with methanol followed by hexane. Pt, 2.7 ± 0.03. Surface platinum by EDAX (on several particles and at several locations after normalizing the average of each particle as one) from 0.68 to 1.24. Surface area 320 m^2/g, Porosity 51%; pores are within 20−70 Å. TEM shows particles with irregular and ill-defined shapes and morphology. **3**: 5% Pt on alumina. Surface area >250 m^2/g. Purchased from Aldrich Chemicals (1998−99, 31,132−4) and used as received.

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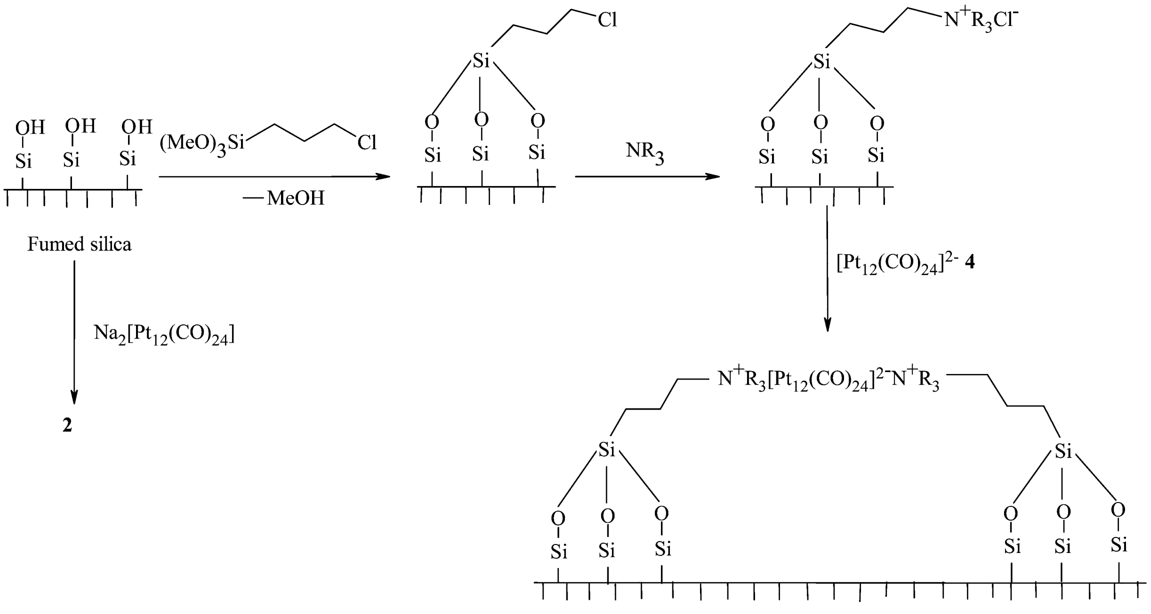
Scheme 1



ties of **1** and **2** was to see if functionalization of the support offers any practical benefits.

As shown in Scheme 1, synthesis of **1** involves treatment of fumed silica first with trimethoxychloropropylsilane followed by triethylamine. The resultant material is then treated with a methanolic solution of the sodium salt of **4** to give **1**. Sample **2** is prepared by a conventional adsorption method, i.e., by taking *unfunctionalized* fumed silica in a methanolic solution of the sodium salt of **4** and then removing the solvent. For meaningful comparison of catalytic activities, the total platinum contents of **1** and **2** are maintained at practically identical levels.[4]

Evidence for the successful incorporation of functional groups and retention of molecular identity of **4** in freshly prepared **1** comes from analytical and spectroscopic [Si^{29} NMR (MAS), IR, and UV−vis] data.[4] The characteristic IR and UV−vis bands of **4** can be clearly seen in freshly prepared **1**. However, the rapid disappearance of ν_{CO} and the charge transfer band indicates that **1** loses all the carbonyl ligands within a few minutes of its preparation. Loss of carbonyl groups from **1** is observed even when it is stored under 1 atm of CO. For sample **2**, the characteristic IR or UV−vis bands of **4** are not seen even with freshly prepared samples. Expectedly, atomic absorption or EDAX analyses show the presence of sodium in **2** but not in **1**. The absence of sodium in **1** is in accordance with the formulation shown in Scheme 1 and implies that an alternative formulation in which one cation is the quaternary ammonium group and the other is a sodium ion, if present at all, would be negligible in concentration. Although the total platinum contents of **1** and **2** are almost identical, the variation in the surface platinum concentration of **2** is significantly more than that of **1**. EDAX analysis of **2** also shows that sodium is present on the surface on average to about 1−3% of the concentration of platinum. Remarkable morphological differences between **1** and **2** are also seen by TEM. Several nanotubes of about 200 nm diameter are found in **1**, while for **2** no such regular shapes are found (Figure 1).

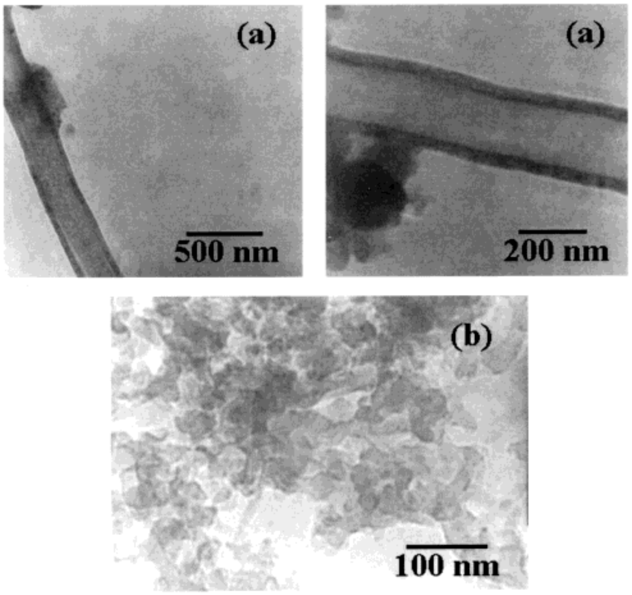


Figure 1. Transmission electron micrographs of (a) **1** and (b) **2**.

The catalytic performances of **1**−**3** have been evaluated for the hydrogenation of cyclohexanone, acetophenone, ethylacetoacetate, and benzonitrile (Table 1). For the same amount of platinum, for all the substrates the percentage conversions with **1** are more than that with either **2** or **3**. The superior activity of **1** can also be clearly seen in Figure 2, where time-monitored conversion plots are shown. The rates of hydrogenation of acetophenone with **1**, **2**, and **3** as catalysts are approximately 5:1.6:1. Similarly the corresponding rates for the hydrogenation of ethylacetoacetate are about 7:2.8:1.

In the literature there are many reports on the hydrogenation of benzonitrile.[5] With **3** as the catalyst total conversion of benzonitrile with selectivity toward

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[5] Nishimura, S. In *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*; John Wiley: New York, 2001; p 254.

Table 1.[a]

substrate	product(s)	catalyst	conversion (%)[c]
ethylacetoacetate	ethyl-3-hydroxy butyrate	**1**	100
		2	76
		3	26
cyclohexanone	cyclohexanol	**1**	69
		2	56
		3	24
benzonitrile[b]	*N*,*N*-dibenzylhydrazine and benzylamine	**1**	90, 10
		2	82, 7
		3	0, 90
acetophenone	1-phenylethanol	**1**	99
		2	62
		3	40

[a] All reactions were carried out with 1 mmol of substrate and 30 mg of **1** or **2**, and 17 mg of **3**, i.e., total platinum for all catalysts 0.84 mg, under 40 bar hydrogen pressure in 1 mL of methanol for 12 h at 300 K unless specified otherwise. All analyses by GC [Shimadzu 14A, SC-30 (mesh 1000−2000) GC column with FID detector]. [b] 15 bar hydrogen pressure, 24 h, 373 K. Analyses by NMR and GC−MS; see ref 6. [c] For benzonitrile the two numbers refer to hydrazine derivative and benzylamine, respectively.

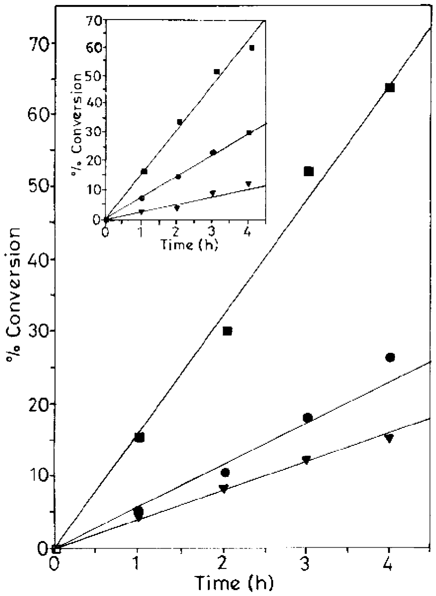

Figure 2. Rate of hydrogenation of acetophenone by **1** (■), **2** (●), and **3** (▼) under 40bar H_2 pressure at 300 K. Inset shows the rate of hydrogenation of ethylacetoacetate. In all the cases the least-squares-fitted straight lines have been drawn only to highlight the differences in the apparent rates and not to suggest that conversion vs time has a linear relationship even when substantial conversion is reached.

benzylamine of >95% is observed. However, under identical conditions with either **1** or **2** as the catalyst, the hydrazine derivative $Ph-CH_2-NH-NH-CH_2-Ph$, characterized by NMR and mass spectrometry, is found to be the main product.[6] With these catalysts the selectivity toward $Ph-CH_2-NH-NH-CH_2-Ph$ lies within 80−90%. The generality of this reaction has been established by using butyronitrile as an additional nitrile substrate. With **1** and **2** as the catalysts 100% conversion with more than 90% selectivity to $C_3H_7-CH_2-NH-NH-CH_2-C_3H_7$ is obtained. In contrast with **3** as the catalyst, total conversion of butyronitrile to butylamine (selectivity 90%) is observed. Structures of many cluster complexes have been reported where the "C−N" moiety of a given organic substrate interacts with more than one metal atom.[7] In the hydrogenation of nitrile with **1** or **2** as the catalyst, similar multimetal activation of the "C−N" moiety as *one of the steps* is likely.

At the end of any catalytic run **1** or **2** could be easily separated by filtration. The reusability of **1** and **2** has also been checked in ethylacetoacetate and benzonitrile hydrogenation reactions by carrying out four successive catalytic runs. No significant difference in terms of catalytic activity or selectivity is observed. Platinum estimation at the end of each run shows that leaching of platinum does not occur.

The catalytic activity of the Chini clusters in the homogeneous hydrogenation reactions of ketones was reported by us long ago[3h] and shown to be zero at temperatures below 313 K. In benzonitrile reduction moderate activity toward benzylamine, rather than phenyl hydrazine formation, was observed. As is apparent from the above discussion, the precise structures of the active sites in **1** and **2** are not known. However, an obvious and important difference between the precursor Chini cluster and **1** and **2** is that in the latter materials the active sites do not have any carbonyl ligands and are probably coordinatively unsaturated. The catalytic performances of the Chini clusters as homogeneous catalysts and **1** and **2** as insoluble supported catalysts are therefore expected to be different, as indeed is found to be the case.

In conclusion we have presented data that show that in ketone hydrogenation reactions in terms of catalytic activity **1** is distinctly superior to *both* **2** and **3**. The data also show that in the hydrogenation of nitriles **1** and **2** have very different chemoselectivity compared to that of the conventional platinum catalyst. Both these observations provide a strong justification for further exploration of the use of carbonyl clusters *and functionalized support* in catalyst preparation.

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(6) Products analyzed by GC−MS technique with a HP-5989 BM MS Engine. The maximum molecular ion peak (*m*/*z*) for $Ph-CH_2-NH-NH-CH_2-Ph$ appears at 211.5 (calculated molecular weight 212). ^1H NMR data: in $CDCl_3$ for $Ph-CH_2-NH-NH-CH_2-Ph$, five aromatic protons (δ, 6.7−8.4 ppm), two CH_2 protons (δ, 3.85 ppm), and one NH proton (δ, 2.0 ppm, disappears on D_2O treatment). The maximum molecular ion peak (*m*/*z*) for $CH_3-CH_2-CH_2-CH_2-NH-NH-CH_2-CH_2-CH_2-CH_3$ appears at 143.5 (calculated molecular weight 144). ^1H NMR data: in $CDCl_3$ for $CH_3-CH_2(c)-CH_2(b)-CH_2(a)-NH-NH-CH_2-CH_2-CH_2-CH_3$, one NH proton ($\delta$, 3.75 ppm, disappears on D_2O treatment), two CH_2(a) protons (δ, 3.45 ppm), two CH_2(b) protons (δ, 2.5 ppm), three CH_3 protons (δ, 1.4 ppm), and two CH_2(c) protons (δ, 0.9 ppm).

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