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A MCM-41-supported platinum carbonyl cluster-derived asymmetric hydrogenation catalyst

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Abstract

Anionic platinum carbonyl cluster has been ion paired with cinchonidium groups that are chemically bound to the surface of MCM-41 and fumed silica. In the hydrogenation of methyl pyruvate or acetophenone the fumed silica-based catalyst gives zero enantioselectivity, but under optimum conditions enantiomeric excesses of > 90 and $\sim 40\%$, respectively, are obtained with the MCM-41-based catalyst.

Keywords: Platinum carbonyl cluster; Hydrogenation catalysts; Functionalized inorganic oxides; Asymmetric catalysis

1. Introduction

Anchoring of homogeneous catalysts to insoluble polymeric supports has been much investigated in the search for a simple and easy method for the separation of catalyst [1–3]. Grafting of proven asymmetric homogeneous catalysts to a solid support is a viable strategy but in most cases requires multistep syntheses of expensive chiral ligands and/or functionalization of a given support with such ligands [3–5]. Another approach that has been the focus of much research avoids the costly synthesis of expensive ligands and/or organometallic complexes. In this approach a conventional heterogeneous catalyst such as platinum or raney nickel is modified by treatment with easily available chiral substances [6–10]. Although the overall success of this approach has been limited, platinum on alumina modified by cinchona alkaloids has been found to be a particularly effective catalyst for the enantioselective hydrogenation of α-ketoesters in general and pyruvate esters in particular (Orito reaction) [6–10].

The potential of Chini clusters as homogeneous catalysts has been investigated by us, and as precursors to supported catalysts by us and by others [11–16]. Very recently we reported hydrogenation of ketones where the Chini cluster $[Pt_{12}(CO)_{24}]^{2-}$, ion paired on functionalized fumed silica, was used as the precatalyst [12]. The superior performance of this catalyst prompted us to explore the potential of analogous but *chiral* materials in the asymmetrical hydrogenation of ketones. We find that an enantioselective catalyst can indeed be obtained with this general method of catalyst synthesis.

Moreover, in view of the recent observations of enhancement of enantioselectivity via constraining chiral asymmetric catalysts within the nanopores of a support, we also investigated the effect of porosity, if any, on the enantioselectivity of our catalysts [17,18]. Our findings establish that the pore size distribution of the support has a critical and remarkable effect. Thus, with fumed silica as the support (see **1** in Scheme 1), no enantioselectivity could be achieved in the hy-

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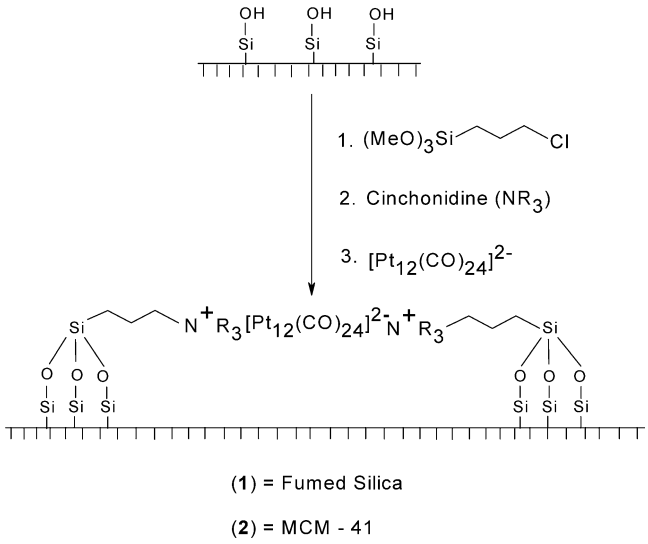

Scheme 1.

drogenation of methyl pyruvate or acetophenone. However, with **2**, a precatalyst with MCM-41 as the support, excellent (∼ 95%) enantiomeric excess is obtained in the Orito reaction, and moderate (∼ 40%) enantioselectivity is achieved for acetophenone.

2. Experimental

All preparations and manipulations were performed with standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures (toluene over Na/benzophenone; methanol over Mg-turnings/iodine), distilled under nitrogen, and used immediately. Chloroplatinic acid was purchased from Johnson Mathey (London). Methyl pyruvate, methyl lactate, cinchonidine, and colloidal silica were purchased from Fluka (Switzerland). Fumed silica, (3-chloropropyl)trimethoxysilane, 1-phenylethanol, and acetophenone were obtained from Aldrich (USA). MCM-41 and $Na_2[Pt_{12}(CO)_{24}]$ were synthesized according to procedures reported in the literature [19,20]. All of the hydrogenation reactions were carried out in an autoclave. Conversions and enantioselectivities of the hydrogenation reactions with different substrates were monitored by a gas chromatographic technique with a FID detector (Shimadzu GC-14A gas chromatograph) and a chiral capillary column (112-2562 CYCLODEXB; J&W Scientific; length 60 m, inner diameter 0.25 mm, film 0.25 µm). All hydrogenated products were initially identified from authentic commercial samples of the expected products.

2.1. Functionalization of fumed silica

Fumed silica was dried at 200 °C under vacuum for 24 h. Dried fumed silica (1 g) was treated with neat (3-chloropropyl)trimethoxysilane (15 ml) at 160 °C in an oil bath for 96 h. It was then filtered and washed thoroughly with toluene followed by methanol. On functionalization the initial white color of the solid support changed to yellow.

2.2. Functionalization of MCM-41

MCM-41 (1 g) preheated under vacuum at 200 °C for 4 h was refluxed with 2 ml of (3-chloropropyl)trimethoxysilane and 20 ml of dry toluene at 160 °C for 160 h. The product was then separated by filtration and washed several times with dry toluene. The ^{29}Si NMR spectra (^{1}H coupling and decoupling) in each step match well with the reported data [21].

2.3. Modification of fumed silica and MCM-41 by cinchonidine alkaloid

The chloropropylsilane-functionalized MCM-41 (1 g) and cinchonidine (0.25 g) were added in a 1:1 absolute ethanol/dry toluene mixture (40 ml). The mixture was heated to reflux at 110 °C for 96 h. It was then filtered and washed thoroughly with dry toluene followed by dry methanol. The same procedure was adopted for the modification of functionalized fumed silica.

2.4. Synthesis of catalysts *1* and *2*

Dried cinchonidine-modified functionalized support (MCM-41 or fumed silica) (1 g) was added in a preformed green methanolic solution (15 ml) of $Na_2[Pt_{12}(CO)_{24}]$ (0.2 g) under a carbon monoxide atmosphere. The mixture was stirred at 25 °C for 48 h (for MCM-41) and 96 h (for fumed silica). The solid material was filtered off and washed thoroughly with dry methanol and then dried under a CO atmosphere.

2.5. Thermal activation of catalysts *1* and *2*

The catalyst **1** or **2** (1 g) was placed in a three-necked round-bottomed flask (25 ml) equipped with nitrogen and vacuum adapters and was flushed with nitrogen to remove any residual oxygen. The system was evacuated and then heated at 70 °C for 4 h under a continuous flow of hydrogen gas. During this process the green color of the catalyst turned to gray. This gray material was used in catalytic experiments with suitable substrates.

2.6. Catalytic experiments with activated catalysts *1* and *2*

All catalytic runs were carried out at 27 °C in 2 ml of methanol contained in glass vials, with 25 to 70 mg of catalysts (**1** or **2**) (∼ 0.75 to 2 mg of platinum) and 0.5 to 2.0 mmol of substrates. The glass vial was placed in an autoclave, and a hydrogen pressure in the range of 20 to 70 bar was applied. At the end of the catalytic run the reaction mixture was subjected to GC, and the extent of conversion was calculated on the basis of the ratio of areas of starting material and the product.

3. Results and discussion

The functionalization of MCM-41 with trialkoxy chloropropylsilane followed by further reactions with amines including ephedrine has been reported [22]. The latter material was used as a potential chiral catalyst in the alkylation of benzaldehyde by diethyl zinc but was found to give only moderate enantioselectivity. The proposed structural formulations of the resultant precatalysts (**1** and **2**) are shown in Scheme 1.

Chemical and EDAX analyses for both **1** and **2** did not show the presence of sodium, ruling out a formulation in which sodium is one of the counter-cations [12]. The powder XRD patterns of **2** and all other MCM-41 derivatives match well with that of the reported pattern of MCM-41 [23]. Surface areas (m^2/g) (by BET) are MCM-41, 740; 2, 470; fumed silica, 240; 1, 100. In **2** and all other MCM-41 derivatives, 90% of the total pore volume comes from pores with radii within the range of 1–2 nm. In **1** and all of the other fumed silica derivatives, 65% of the total pore volume comes from pores with radii within the range of 2–8 nm. See Fig. 1b for the characteristic fringes of MCM-41.

Chemical analyses show that in **1** and **2** the contents of chloropropyl, cinchonidine, and platinum are similar, and approximately 2, 0.5, and 0.2 mmol/g, respectively. The observed nitrogen and platinum values indicate that less than one-tenth of the tetralkylammonium functionalities on the surface are used in ion pairing. Freshly prepared **1** and **2** have IR (2060 and 1850 cm^{-1}) and UV–vis (reflectance, 620 nm) bands that match well with that of $[Pt_{12}(CO)_{24}]^{2-}$ [24]. However, as is evident from the disappearance of the characteristic IR and UV–vis bands, the CO ligands are lost quickly (< 10 min), even when **1** and **2** are stored under CO. The formulations shown in the scheme for **1** and **2** are therefore applicable only to the materials before the CO loss and their use as catalysts. It may be noted that although retention of the cluster framework by the decarbonylated Chini cluster in zeoliteY has been reported, the decarbonylated species is known to undergo aggregation on MgO [14–16].

In the X-ray photoemission spectrum of **1** and **2**, platinum $4f$ core levels are clearly observed (see Fig. 1a). The broadening and small valley between the spin-orbit components clearly indicates that two different Pt species are present. Deconvolution shows the two different species at 71 and 72.7 ± 0.1 eV with an intensity ratio of 5:1, respectively. The high-intensity signal has a binding energy (BE) close to that of the reported value [13,25] for the free platinum cluster ($4f_{7/2} \sim 71.0$ eV). The high-BE component is due to a Pt^{2+}

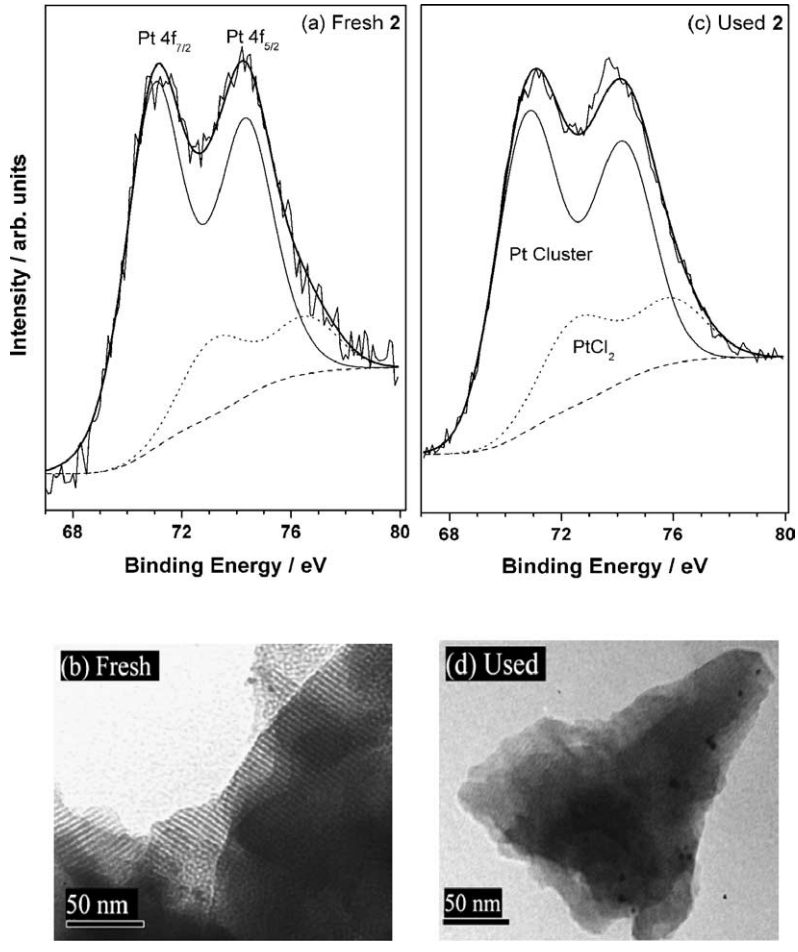

Fig. 1. X-ray photoemission spectra of Pt $4f$ of **2** (a, before and c, after catalysis). Transmission electron micrographs of **2** (b, before and d, after catalysis).

species, probably $PtCl_2$ with coordinated organic moieties. Facile decarbonylation of the supported cluster is expected to cause a slight shift in the platinum BE. Reaction between a small fraction of the decarbonylated clusters and excess tetralkyl ammonium chloride functionalities on the support probably lead to the formation of $PtCl_2$. Transmission electron micrographs (TEMs) of freshly prepared **1** and **2** have also been recorded. They show characteristic fringes typical of MCM-41 for **2**. Well-dispersed decarbonylated platinum clusters or nanoparticles in the pores of MCM-41 should be smaller (< 2 nm) than the fringe width (3.5 nm) and hence should not be observed. Nonetheless, it suggests a uniform distribution of platinum sites in the pores (see Fig. 1b).

Control experiments established that in solution, in the presence or absence of cinchonidine, $[Pt_{12}(CO)_{24}]^{2-}$ as a homogeneous catalyst has zero activity for the hydrogenation of methyl pyruvate or acetophenone. In contrast, **1** and **2** show good activity for both substrates. Depending on the reaction conditions, turnovers ranging from 100 to 50 h^{-1} may be achieved for both substrates. Preliminary rate measurements on the hydrogenation of methyl pyruvate with both catalysts have been carried out. Rates are found to be approximately linearly related to the concentrations of the catalysts and methyl pyruvate (Fig. 2), but a complex rate dependence on hydrogen pressure is observed.

The enantioselectivities of **1** and **2**, if any, have been measured under a wide range of conditions (see Section 2.6). With **1** as the catalyst we never observed any enantioselectivity for methyl pyruvate or for acetophenone hydrogenation. In contrast, with **2** as the catalyst for both substrates, varying enantioselectivities are obtained. In the Orito reaction, cinchona-modified commercial catalysts are known to give maximum enantioselectivity and rate only after a certain induction time [6]. With **2** as the catalyst for both acetophenone and methyl pyruvate, there is no such induction time. However, the best enantioselectivities for both substrates are obtained under relatively low conversions. Thus, for methyl pyruvate under optimum conditions $\sim$ 95% ee is obtained, but enantioselectivity decreases rapidly with increasing conversion (see Fig. 2). Similar results are obtained in the hydrogenation of acetophenone, where $\sim$ 40 and 15% ee are obtained at $\sim$ 10 and 40 turnovers, respectively.

Both **1** and **2** have been recycled three times without any noticeable drop in percentage conversion. The loss in enantioselectivity of **2** with increased conversion is irreversible, and low enantioselectivities are observed for the second and third runs. Both XPS and TEM analyses of **2** after its use as a catalyst show differences from the fresh material (Figs. 1c and d). In XPS the electron count of the used catalyst is noticeably greater than that of the fresh catalyst. This indicates that although in **2**, before its use as a catalyst, the platinum clusters are well dispersed within the pores, during catalysis agglomeration of platinum clusters takes place. Also under hydrogenation conditions some $PtCl_2$ is reduced to metallic platinum. Further evidence for platinum agglomeration comes from TEM, where larger platinum particles (3–6 nm)

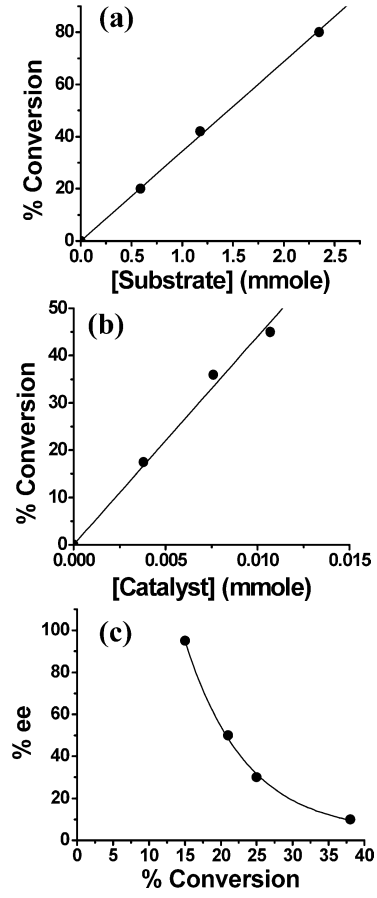

Fig. 2. (a) Substrate (MPV) concentrations vs. conversion plot (%) for **2**. Hydrogen pressure, 50 bar; catalyst quantity, 70 mg. (b) Catalyst (**2**) concentration vs. conversion plot (%). Amount of MPV used, 120 mg (1.175 mmol); hydrogen pressure, 50 bar. (c) Conversion (%) versus ee plot (%) for **2**. For reaction conditions see Experimental section.

can clearly be seen at the edges/grain boundaries of the used catalyst. However, there is no significant difference in the BE of the fresh and used catalysts.

The loss in enantioselectivity of **2** with increased conversions must be due to the conversion of the enantioselective sites to nonselective sites. The agglomeration of the platinum clusters at the edges/grain boundaries of the used catalyst means that the decarbonylated clusters are capable of moving away from their original chiral environment. The clusters that are confined within the narrow pores of MCM-41 are expected to be less mobile and more resistant to agglomeration than those confined in the larger pores of fumed silica. This probably is the reason for the remarkable difference in the effect of the support on enantioselectivity.

4. Conclusion

In conclusion, we have shown that by ion pairing $[Pt_{12}(CO)_{24}]^{2-}$ with cinchonidium groups chemically linked to the surface of MCM-41, we obtained an asymmetric hydrogenation catalyst. An analogous material with fumed silica

as the support does not give any enantioselectivity, indicating that the pore size distribution of MCM-41 is of critical importance. Research aimed at the enhancement of enantioselectivity under high conversion, through the optimization of degree of functionalization and pore size distribution, is currently under way.

Acknowledgment

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References

[1] M. Lemaire, Pure Appl. Chem. 76 (2004) 679.
[2] P. McMorn, G.J. Hutchings, Chem. Soc. Rev. 33 (2004) 108.
[3] C.E. Song, S. Lee, Chem. Rev. 102 (2002) 3495.
[4] P.N. Liu, P.M. Gu, F. Wang, Y.Q. Tu, Org. Lett. 6 (2004) 169.
[5] J.M. Thomas, B.F.G. Johnson, R. Raja, G. Sankar, P.A. Midgley, Acc. Chem. Res. 36 (2003) 20.
[6] M. Studer, H.-U. Blaser, C. Exner, Adv. Synth. Catal. 345 (2003) 45, and references therein.
[7] H.-U. Blaser, H.-P. Jalett, M. Müller, M. Studer, Catal. Today 37 (1997) 441.
[8] A. Baiker, J. Mol. Catal. A 163 (2000) 205.
[9] M. Studer, S. Burkhardt, A.F. Indolese, H.-U. Blaser, Chem. Commun. (2000) 1327.
[10] M. von Arx, T. Mallat, A. Baiker, Angew. Chem. Int. Ed. 40 (2001) 2302.
[11] H. Paul, S. Basu, S. Bhaduri, G.K. Lahiri, J. Organomet. Chem. 689 (2004) 309.
[12] H. Paul, S. Bhaduri, G.K. Lahiri, Organometallics 22 (2003) 3019.
[13] S. Bhaduri, K.R. Sharma, J. Chem. Soc., Dalton Trans. (1984) 2309.
[14] J.G.-C. Shen, J. Phys. Chem. B 104 (2000) 423.
[15] G. Sastre, N. Raj, C.R.A. Catlow, R. Roque-Malherbe, A. Corma, J. Phys. Chem. B 102 (1998) 3198.
[16] J.-R. Chang, D.C. Koningsberger, B.C. Gates, J. Am. Chem. Soc. 114 (1992) 6460.
[17] R. Raja, J.M. Thomas, M.D. Jones, B.F.G. Johnson, D.E.W. Vaughan, J. Am. Chem. Soc. 125 (2003) 14982, and references therein.
[18] M.D. Jones, R. Raja, J.M. Thomas, B.F.G. Johnson, D.W. Lewis, J. Rouzaud, K.D.M. Harris, Angew. Chem. Int. Ed. 42 (2003) 4326.
[19] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[20] G. Longoni, P. Chini, J. Am. Chem. Soc. 98 (1976) 7225.
[21] E.J.R. Sudhölter, R. Huis, G.R. Hays, N.C.M. Alma, J. Colloid Interface Sci. 103 (1985) 554.
[22] T.M. Jyothi, M.L. Kaliya, M. Herskowitz, M.V. Landau, Chem. Commun. (2001) 992.
[23] R. Mokaya, Chem. Commun. (2001) 1092.
[24] S. Bhaduri, G.K. Lahiri, D. Mukesh, H. Paul, K. Sarma, Organometallics 20 (2001) 3329.
[25] G. Apai, S.-T. Lee, M.G. Mason, L.J. Gerenser, S.A. Gardner, J. Am. Chem. Soc. 101 (1979) 6880.