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Is a naked platinum nanocatalyst better than the analogous supported catalysts?†

Abhishek Dutta Chowdhury, Sumit Bhaduri* and Goutam Kumar Lahiri*

The performance of naked nanocatalyst 1, derived from Chini cluster ($[Pt_{15}(CO)_{30}]^{2-}$), has been evaluated with special reference to the analogous catalysts 2 and 3 which were derived from the same $[Pt_{15}(CO)_{30}]^{2-}$ but supported by MCM-41 and the water soluble polymer PDADMAC, respectively.
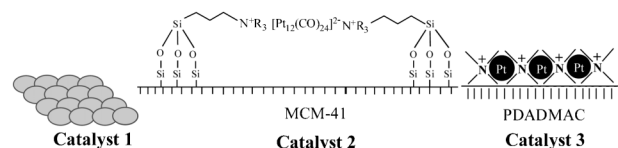
The shape and size of metal nanoparticles (NPs) are known to vary considerably depending on their synthetic procedure; particularly the nature of the metal precursors and the stabilizers. The shape and size also have a direct bearing on the performance of such nanoparticles as catalysts.[1] In this context, a wide variety of supported, stabilized or capped platinum nanoparticles (Pt-NPs) have been tested, and it has been demonstrated that the preparative procedures used have notable effects on their catalytic performances.[1–7] The well known Orito reaction *i.e.* the enantio-selective hydrogenation of α-ketoesters has been extensively investigated by Baiker *et al.*, other groups and us using various organic and inorganic supported Pt-nanocatalysts modified with chiral cinchona alkaloids.[2–5] Recently, Baiker *et al.* have shown that the acid–base properties of the organic stabilizer or the inorganic support exert a remarkable effect on the diastereoselec-tivity of the catalysts in the hydrogenation of the heteroaromatic ring of cinchonidine.[5] In view of this, further explorations are needed to tune the morphology of Pt-NPs and their subsequent performance.

We reported the performance of Pt-NPs derived from Chini clusters ($[Pt_{15}(CO)_{30}]^{2-}$) supported by functionalized MCM-41 (catalyst 2)[4] and water soluble polydiallyldimethyl ammonium chloride (PDADMAC) (catalyst 3)[6,7] (Scheme S1†). While 2 with the chiral modifier Cd (Cd = cinchonidine free base) exhibited enantioselectivity in the hydrogenation of methyl pyruvate (MPV), 3, unlike other reported colloidal Pt-catalysts, did not show any enantioselectivity.[4,6] On the contrary, catalyst 3 was found to be an efficient oxidation catalyst for primary and secondary alcohols, but catalyst 2 was inactive.[7]

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India. E-mail: lahiri@chem.iitb.ac.in
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Catalyst 1   **Catalyst 2**   **Catalyst 3**

Thus, for a comprehensive evaluation of the performance of $[Pt_{15}(CO)_{30}]^{2-}$ derived nanocatalysts, the elimination of the effects arising from the supports is necessary. To achieve this objective, the naked Pt-NPs (catalyst 1) have been synthesized directly from a DMF solution of $(^tBu_4N)_2[Pt_{15}(CO)_{30}]$ at ∼100 °C without using any base, surfactant or stabilizer (Scheme S1†), and their catalytic potential has been explored. DMF here functions as a solvent as well as a reducing agent, as it does in the reported synthesis of naked gold nanoparticles.[8] Liz-Marzán *et al.* have also reported the role of DMF as a powerful reductant in developing Ag nanocrystals where the reduction rate enhances remarkably as the temperature increases. However, the reaction temperature was maintained at ∼100 °C for relatively slow and steady growth of the metal NPs.[9]
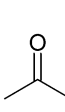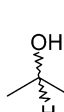
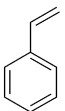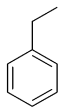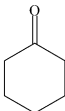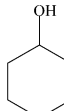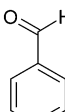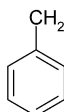The absence of a carbonyl group in 1 was shown by IR-spectroscopy (Fig. S1†). The efficiency of 1 for the hydrogenation of various unsaturated organic functionalities was evaluated, includ-ing the enatioselective hydrogenation of methyl pyruvate (MPV) after modification with Cd. The results were compared with those reported earlier for the supported analogues, 2 and 3. Furthermore, 1 modified with Cd was used for the oxidation of methyl lactate (ML) which leads to the first successful example of oxidative kinetic resolution using a chirally modified heteroge-neous catalyst. It may be noted that although significant advancements have been made in the specialized field of asymmetric synthesis, the resolution of racemates is still the main industrial approach for the synt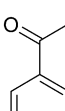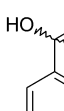hesis of chiral compounds. Thus, the non-enzymatic kinetic resolution of racemic compounds by chiral catalysts is an important area of synthetic organic chemistry.[10]

TEM studies of fresh 1 reveal a chain-like structure of Pt-NPs where majority of the particles (*ca.*70%) lie within a size range of 2–3 nm (Fig. S2†). The formation of discrete Pt-NPs instead of Pt-nanowire or chains has been reported for supported 2 (size <3

Table 1 Comparative hydrogenation data for **1–3**

Substrate	Product	**1**[a] % conv.	**1**[a] TOF (h⁻¹)	**2**[b] TOF (h⁻¹)	**3**[c] TOF (h⁻¹)
(styrene)	(ethylbenzene)	100	666	521	98
(cyclohexanone)	(cyclohexanol)	100	666	15.8	197
(benzaldehyde)	(benzyl alcohol, CH₂OH)	95	633	99	190
(acetophenone)	(1-phenylethanol, HO–H)	25	166	45.5	42
(methyl pyruvate)	(methyl lactate, OH)	100[d]	83	71.4	122

[a] Reaction conditions: catalyst **1** : substrate = 1 : 1000, solvent: MeOH, hydrogen pressure: 50 bar, temperature: 298 K, sonication time: 30 min, reaction time: 90 min, analyzed by GC using *n*-dodecane as an external standard, TOF = turnover frequency (turnover number/time). See ESI† for details. [b] Catalytic data of catalyst **2** (ref. 4). [c] Catalytic data of catalyst **3** (ref. 6). [d] Reaction time: 12 h.

Table 2 Enantioselective hydrogenation of methyl pyruvate by **1**[a]

Substrate	Product	Solvent (ε)	Time (min)	% conv.	ee
MPV	(R/S) ML	MeOH (33.6)	15	55	45
			30	71	70
			60	100	76
		Toluene (2.38)	15	70	85
			30	100	79
		Cyclohexane (2.02)	30	76	76
		Chlorobenzene (5.71)	30	72	61
		CH₂Cl₂ (9.08)	30	8	15

[a] Reaction conditions: catalyst **1** : MPV = 1 : 100, substrate : Cd = 10 : 1, hydrogen pressure: 50 bar, temperature: 300 K, sonication time: 30 min, analyzed by GC, See ESI† for details. ε = dielectric constant, acidic or basic solvents are not used. R-ML is the major product. The *ee* value decreases by about 60% after the first catalytic run.

nm) and **3** (size ∼2–8 nm).[4–6] The selective growth of a chain-like structure of the Pt-NPs in **1** could be attributed to the difference in diffusional mobilities of the particles on a support (MCM-41 or PDADMAC) and in DMF solution.

In order to achieve maximum conversion, sonication of a methanolic suspension of **1** is required prior to each catalytic run, as it introduces homogeneity in the particle size distribution. The positive effect of ultrasonication on the performance of the catalyst has also been demonstrated previously.[11] The chemoselective hydrogenation data of substrates **1–3** are listed in Table 1 and Table S1.† It is clear that **1** gives a higher turnover frequency (TOF; turnover number/time) in almost all cases as compared to **2** or **3**.[4,6] As full conversion is achieved for styrene, cyclohexanone and methyl pyruvate, the calculated TOF for **1** refers to the lowest limits. It should be emphasized that even on the removal of the support, **1** retains its chemoselectivity, and interestingly activity is enhanced in comparison to supported versions **2** or **3**. Though **1–3** efficiently catalyze the hydrogenation of alkene and carbonyl functionalities, the aromatic ring or the ester group remains unreduced. From recycling experiments it is clear that conversion (%) decreases a little after the first catalytic run, and to an appreciable extent after the second run (Table S2†) due to the rapid agglomeration of the particles. The TEM micrographs of **1** show the growth of the particles from 2–3 nm (fresh) to 6–8 nm (Fig. S3†) after the second catalytic run.

Catalyst **1** also exhibits the general characteristics of Orito catalysts such as the solvent dependence of *ee*, the complex effect of the cinchona modifiers on the enantioselectivity and rate acceleration in the presence of Cd. Though there is no direct correlation between *ee* and the dielectric constant of the solvent for the enantioselective hydrogenation of MPV by the Cd modified catalyst **1**, the highest *ee* is obtained in toluene and modest and drastic reductions in *ee* are observed in chlorobenzene and dichloromethane, respectively (Table 2).

Though the chiral modifier (cinchonidine) introduces enantioselectivity, other modifiers such as cinchonine, quinidine and quinine are found to be ineffective. It should be noted that unlike **1** and **2**, **3** did not show any enantioselectivity for the MPV to ML transformation,[4,6] possibly due to the insolubility of the chiral modifiers in water. Turnover frequencies (TOF) for the conversion of MPV to ML after 15 min in methanol and toluene for **1** of 3.7 and 4.7 min⁻¹, respectively, are significantly higher than the range of 2.1–2.6 min⁻¹ obtained for **2** and **3**.[4,6] Also in the presence of Cd, an increase in TOF (≈17%) is observed for **1** in methanol (Tables 1 and 2).

However, contrasting behavior between **1** and **2** is observed with respect to the change of *ee* with time. With **2**, high *ee* (≈90%) can be achieved at very low (10–15) turnovers and with an increase in TON, *ee* drastically drops to the racemic state.[4] On the other hand, with **1** as the catalyst and Cd as the chiral modifier appreciable *ee* (⩽79%) with a high TON (turnover number) is obtained, where *ee* increases with the increase in conversion (Fig. S4†). The (111) face of the Pt-NPs in **1** has been shown to give the best enantioselectivity (Fig. S2; see ESI† for additional discussion).[3,4] The kinetic modeling and TEM studies of **2** reported earlier revealed that under hydrogen pressure the considerable mobility of the Pt-NPs on the MCM-41 surface led to the migration of the Pt-NPs away from the chiral Cd⁺ sites followed by the

Table 3 Catalytic oxidation of methyl lactate[a]

Substrate	Product	Catalyst	Solvent	Time (hr)	% conv.	% ee
(R)/(S)-ML	MPV	**1**	H_2O	40	60	—
			MeOH : H_2O (1 : 5)[b]	40	58	50
S-ML	MPV	**1**	H_2O	40	58	—
			MeOH : H_2O (1 : 5)[b]	40	52	0
S-ML	MPV	**3**	H_2O	20	<5	—
S-ML	MPV	Pt/C, Pt/Al$_2$O$_3$, Pt/TiO$_2$	H_2O	20	0	—

[a] Reaction condition: Catalyst : ML = 1 : 85, oxidant: O_2, temperature: 353 K , sonication time: 30 min, reaction mixture was extracted by ethyl acetate and analyzed by GC using dodecane as an external standard. See ESI† for details. [b] ML : Cd = 10 : 1.

agglomeration of particles, causing a drastic drop in enantioselectivity with time.[4] The superior catalytic activity of **1** could be attributed to its bare nature which facilitates its direct mode of interaction with the substrate/additive (Fig. S5–S7†). Also, sonication prior to each catalytic experiment provides homogeneously distributed naked Pt-NPs (**1**) for such interactions. However, this is not feasible for the supported catalysts (**2** or **3**); either the particles are hindered within the pore of MCM-41 (for **2**) or crowded by bulky organic PDADMAC supports (for **3**). In essence, catalytic activity and selectivity suggest that naked **1** is a much better catalyst than its supported analogue **2** or **3**.

Unfortunately the enantioselectivity decreases after the first catalytic run, which can be attributed to (i) the loss of the Pt (111) face from the active catalytic sites, (ii) the increase in particle size (5–6 nm after the first run) and (iii) the change in morphology (Fig. S1–S7†).

Furthermore, catalyst **1** exhibits good activity and selectivity for the hydrogenation of o-CNB and p-CNB, and for m-CNB (CNB = chloronitrobenzene) it shows relatively low activity with reasonable selectivity (Table S3†). In general, as compared to **3**,[6] **1** is found to be more efficient for the hydrogenation of various CNBs. The relatively small particle size and specific orientation of Pt-NPs in **1** presumably make them more accessible for substrate–nanoparticle interaction, which is essential for the selective hydrogenation of CNBs (Scheme S2†). It should be noted that here the primary objective is to maximize the yield of pharmaceutically important chloroanilines (CAN) by evading the dehydrohalogenation of CNB.[12]

The resolution of racemic mixtures has been considered to be a convenient approach for the large scale preparation of enantiopure compounds. This has been achieved biologically by hydrolytic enzymes such as lipases and esterases.[13] In this regard maximum success has been obtained under homogeneous conditions.[14] Surprisingly, there are no reports in the literature to date regarding the oxidative kinetic resolution of racemic ML using Orito type heterogeneous catalysts. Commercial Pt-catalysts with different supports failed to show any observable activity (Table 3). In the ML oxidation reaction **3** is almost and **2** is totally inactive whereas **1** shows appreciable activity (Table 3). Cd modified **1** catalyzes the oxidation of racemic ML to MPV with kinetic resolution (ee ≤ 50%) using molecular oxygen with R-ML as the major enantiomer. Time monitored conversion and enantioselectivity data show that both conversion and ee increase gradually with time and ∼50% ee being achieved with about 58%

conversion (Fig. S8†). Control experiments show that catalyst **1** in the presence or absence of Cd does not catalyze the racemization of optically pure ML and thus β-hydride elimination is believed to be the most probable mechanistic route for the reverse Orito reaction (Scheme S3†).

In conclusion, the performance of catalyst **1** has been compared with the analogous supported catalysts **2** and **3** and significant differences have been observed. Thus, catalytic activity improves remarkably upon the elimination of the effect of the supports, which offers an alternative, convenient and rather more environmentally benign option for dealing with various problems in the field of heterogeneous catalysis.[15] Unlike usual Pt-catalysts, the naked Pt-nanocatalyst **1** facilitates a wide variety of hydrogenation as well as oxidation reactions without any further modification under environmentally benign reaction conditions, which essentially makes it a unique and versatile heterogeneous catalyst. Further improvements in this direction, particularly the reverse Orito reaction with the naked nanoparticles, are in progress.

Acknowledgements

Notes and references

1 (a) C. A. Witham, W. Huang, C.-K. Tsung, J. N. Kuhn, G. A. Somorjai and F. D. Toste, *Nat. Chem.*, 2010, **2**, 36; (b) C. Burda, X. B. Chen, R. Narayanan and M. A. El-Sayed, *Chem. Rev.*, 2005, **105**, 1025; (c) N. L. Rosi and C. A. Mirkin, *Chem. Rev.*, 2005, **105**, 1547.

2 (a) B. Török, A. Kulkarni, R. DeSousa, K. Satuluri, M. Török and G. K. Surya Prakash, *Catal. Lett.*, 2011, **141**, 1435; (b) T. Burgi and A. Baiker, *Acc. Chem. Res.*, 2004, **37**, 909; (c) E. N. Jacobsen, A. Pfaltz and H. Yamamoto, *Comprehensive Asymmetric Catalysis*, Springer: Berlin, 1999, vol. 1–3.

3 (a) A. Baiker, *J. Mol. Catal. A: Chem.*, 2000, **163**, 205; 1997, **115**, 473; (b) N. Künzle, R. Hess, T. Mallat and A. Baiker, *J. Catal.*, 1999, **186**, 239; (c) A. Vargas, T. Bürgi and A. Baiker, *J. Catal.*, 2004, **226**, 69; (d) T. Bürgi, F. Atamny, R. Schlögl and A. Baiker, *J. Phys. Chem. B*, 2000, **104**, 5953.

4 (a) S. Basu, H. Paul, C. S. Gopinath, S. Bhaduri and G. K. Lahiri, *J. Catal.*, 2005, **229**, 298; (b) S. Basu, M. Mapa, C. S. Gopinath, D. Mukesh, S. Bhaduri and G. K. Lahiri, *J. Catal.*, 2006, **239**, 154.

5 (a) E. Schmidt, W. Kleist, F. Krumeich, T. Mallat and A. Baiker, *Chem.–Eur. J.*, 2010, **16**, 2181; (b) E. Schmidt, F. Hoxha, T. Mallat and A. Baiker, *J. Catal.*, 2010, **274**, 117.

6 (a) P. Maity, S. Basu, S. Bhaduri and G. K. Lahiri, *Adv. Synth. Catal.*, 2007, **349**, 1955; (b) P. Maity, S. Basu, S. Bhaduri and G. K. Lahiri, *J. Mol. Catal. A: Chem.*, 2007, **270**, 117.

7 P. Maity, C. S. Gopinath, S. Bhaduri and G. K. Lahiri, *Green Chem.*, 2009, **11**, 554.

8 G. H. Jeong, M. Kim, Y. W. Lee, W. Choi, W. T. Oh, Q.-H. Park and S. W. Han, *J. Am. Chem. Soc.*, 2009, **131**, 1672.

9 I. Pastoriza-Santos and L. M. Liz-Marzán, *Langmuir*, 1999, **15**, 948; Nano Lett., 2002, **2**, 903.

10 (a) H. Pellissier, *Adv. Synth. Catal.*, 2011, **353**, 1613; (b) H. Becker and K. B. Sharpless, *Asymmetric Oxidation Reactions: A Practical Approach in Chemistry* ed. T. Katsui, Oxford University Press: New York, 2001.

11 (a) B. Torok, K. Felfoldi, G. Szakonyi, K. Balázsik and M. Bartók, *Catal. Lett.*, 1998, **52**, 81; (b) K. Balázsik, K. Felfoldi and M. Bartók, *Ultrason. Sonochem.*, 2001, **8**, 191.

12 (a) A. Indra, P. R. Rajamohanan, C. S. Gopinath, S. Bhaduri and G. K. Lahiri, *Appl. Catal., A*, 2011, **399**, 117, and the references therein; (b) A. Corma, S. Iborra, F. X. L. Xamena, R. Monton, J. J. Calvino and C. Prestipino, *J. Phys. Chem. C*, 2010, **114**, 8828.

13 (a) C. Neri, R. J. Parker and J. M. J. Williams, *Enzyme Catalysis in Organic Synthesis*, Wiley-VCH, Weinheim, 2002, pp 287; (b) M. Bakker, A. S. Spruijt, F. vanRantwijk and R. A. Sheldon, *Tetrahedron: Asymmetry*, 2000, **11**, 1801.

14 (a) K. Yamaguchi, T. Koike, M. Kotani, M. Matsushita, S. Shinachi and N. Mizuno, *Chem.–Eur. J.*, 2005, **11**, 6574; (b) Y. Zhu, K.-L. Fow, G.-K. Chuah and S. Jaenicke, *Chem.–Eur. J.*, 2007, **13**, 541; (c) S. Wuyts, K. de emmerman, D. E. de Vos and P. A. Jacobs, *Chem.–Eur. J.*, 2005, **11**, 386.

15 (a) R. Hudson, A. Rivière, C. M. Cirtiu, K. L. Luska and A. Moores, *Chem. Commun.*, 2012, **48**, 3360; (b) R. Hudson, C. J. Li and A. Moores, *Green Chem.*, 2012, **14**, 622.