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Mesitylene solvated platinum atoms in the preparation of efficient supported catalysts for the dehydrogenation of methylcyclohexane to toluene

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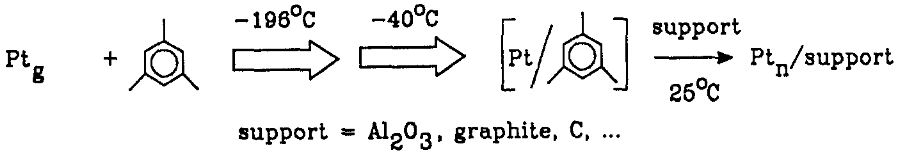
Mesitylene solvated platinum atoms have been conveniently used for the deposition of active Pt particles on γ-Al_2O_3 supports. The so prepared catalysts have been compared with traditionally obtained Pt/γ-Al_2O_3 catalysts in the dehydrogenation of methylcyclohexane to toluene, at 200 and 250°C, showing, at low Pt loadings, a much greater specific activity.

Keywords: Platinum atoms; platinum deposition; methylcyclohexane dehydrogenation

Solvated metal atoms obtained by reaction of transition metal vapour with weakly stabilizing ligands are useful and original reagents for the deposition of active metal clusters onto catalyst supports [1]. The method ensures the placing of small metal particles in their reduced state and no activation steps are necessary: many metal–ligand combinations can be used, and the choice of ligands can be rightly overseen in order to exert a valuable control over metal clusters size [2].

We found that mesitylene is a very suitable ligand, more convenient than the already employed toluene [3], to stabilize Pt atoms; as often observed in arene transition metal chemistry, it could be due to a stronger metal–ligand interaction, as result of the presence on the ligand of more, electron donating, methyl groups [4]. The cocondensation of Pt vapour and mesitylene affords products soluble in the excess of mesitylene, stable at relative low temperature ($-20/0$°C), while the analogous Pt/toluene cocondesates rapidly decomposed at -70°C. The "mesitylene solvated Pt atoms" gently react with support such as Al_2O_3, C, graphite, ..., depositing active Pt particles, under very mild conditions [5] (scheme 1).



Scheme 1.

In a typical experiment platinum vapour (80–100 mg), obtained by resistive heating of a W wire surface coated with electrodeposited Pt [6], was cocondensed at liquid nitrogen temperature with mesitylene (40 ml) in a glass reactor [7]. The flask was warmed to −20°C and the resulting yellow-brown solution siphoned under argon and handled using Schlenk tube technique. By treating the support, such as γ-Al_2O_3, graphite, carbon, with the above solution and on warming to room temperature, Pt particles are deposited and the solution readily turns clear. Samples at different Pt contents (0.1–0.01) have been prepared, the amount of Pt in the starting solution being determined by X-ray fluorescence [8]. The aim was to prepare a low loaded noble metal catalyst with a very high metal dispersion and a remarkable reactivity.

The catalytic activity of so prepared Pt/γ-Al_2O_3 systems has been evaluated in the dehydrogenation of methylcyclohexane (MCH) to toluene and compared with that of conventional Pt reforming catalysts. Catalytic measurements were performed by using a pulse microreactor consisting of a stainless steel tube placed in the vaporization chamber of a gas-chromatograph. Conventional reforming catalysts were reduced in situ under flowing hydrogen at 400°C for 1 h while Pt vapour derived systems have been tested without any activation pretreatment. The methylcyclohexane (MCH) dehydrogenation was studied at 200–250°C by injecting 1 μl pulses of MCH. No products other than toluene were detected. The activity data were recorded after a fixed number of pulses [6–8] had been injected. No catalyst deactivation has been observed during the sequence of pulses. All the catalysts exhibited an excellent stability under the reaction conditions adopted.

In table 1 are summarised the activity data of the investigated catalysts in terms of percentage MCH conversion and specific activity (10^{-4} g MCH conv./mg Pt). It can be seen that, at 250°C, the mesitylene solvated Pt derived catalysts show a remarkable activity. Samples of Pt/γ-Al_2O_3, containing 0.1% of Pt give a conversion of $\approx$ 34.4% with a specific activity (10^{-4} g MCH/mg Pt) of $\approx$ 48. Using Pt/Al_2O_3 catalysts at lower Pt contents (0.01%) the conversion is $\approx$ 21% with a specific activity of $\approx$ 166. Under the same reaction conditions the catalytic activity of Pt/γ-Al_2O_3 systems conventionally prepared starting from H_2PtCl_6 [9], is remarkably lower. Samples containing 0.16 wt% of Pt show a specific activity at 200°C of $\approx$ 2.5, and of $\approx$ 12 at 250°C, while catalysts with Pt loading of $\approx$ 0.01 wt% are nearly powerless; the γ-Al_2O_3, by itself, is

Table 1
Methylcyclohexane dehydrogenation using different Pt catalysts [a]

Catalyst [b] (Pt wt%)	Temperature (°C)	Conversion (%)	Specific activity (10^{-4} g MCH/mg Pt)
Pt/Al_2O_3	200	6.50	9.90
(0.1%)	250	34.40	48.10
Pt/Al_2O_3	200	3.40	26.15
(0.01%)	250	21.60	166.10
Pt/Al_2O_3 (conv.)	200	2.70	2.59
(0.16%)	250	13.20	12.69
Pt/Al_2O_3 (conv.)	200	0.17	2.40
(0.01%)	250	0.56	7.80
γ-Al_2O_3	200	–	–
	250	0.09	–

[a] Runs performed using a pulse microreactor consisting of a stainless steel tube of $l = 80$ mm and i.d. = 4 mm, containing 0.05–0.1 g of catalyst diluted with carborundum (1/20 vol/vol); pulses of 1 μl; N_2 (50 ml/min) as carrier gas.

[b] Al_2O_3: γ-Al_2O_3 AKZO 000-1.5E, calcined in air at 500°C; conventional (conv.) Pt/γ-Al_2O_3 catalysts prepared by impregnation of γ-Al_2O_3 support with hydrochloric solution of H_2PtCl_6 and subsequent drying at 110°C and calcination in air at 500°C.

inefficient in the above reaction. Although the activity scale is still valid at temperature higher than 250°C, the catalytic activity has been evaluated at 200–250°C in order to avoid thermodynamic equilibrium constraints.

Preliminary catalyst characterization by TEM and hydrogen chemisorption has been undertaken. The metal surface area (MSA) and the Pt average particle size (d) of the studied catalysts are given in table 2. The values of d determined by TEM are slightly higher than those obtained by hydrogen chemisorption. This could be due to the assumption of the chemisorption stoichiometry ratio $H:Pt_s$ of 1 : 1. On the whole, such values of d indicate that our low loaded Pt catalysts prepared either by Pt vapour deposition or conventional procedures are highly dispersed. As a possible explanation of the higher specific activity of Pt vapour derived catalysts one could consider that in samples prepared from H_2PtCl_6 oxidated Pt species are probably still present [10]. In fact, at so low Pt loadings it could play a crucial role in lowering the catalytic activity. However, eventual differences in the extent of structural faults or the preferential exposure of the higher reactive planes could also account for the different reactivity of the above Pt catalysts.

In order to get a deeper insight in the phenomenon, studies on the deposition of Pt particles on other supports and on the catalytic activity of the resulting systems have been initiated. Preliminary results indicate that Pt/carbon systems, prepared as described for the Pt/γ-Al_2O_3 samples, are also active in the

Table 2

Hydrogen chemisorption and TEM characterization of Pt catalysts

Catalyst	Metal surface area [a] $m^2_{Pt}\ g^{-1}_{Pt}$	d_{Chem} [b] (Å)	d_{TEM} [b] (Å)
0.1 wt% Pt/γ-Al_2O_3 (Pt vapour derived)	193	15	20
0.16 wt% Pt/γ-Al_2O_3 (conventional)	199	15	25
0.01 wt% Pt/γ-Al_2O_3 (Pt vapour derived)	245	11	– [c]
0.01 wt% Pt/γ-Al_2O_3 (conventional)	192	15	– [c]

[a] Calculated from the chemisorption data assuming that the Pt particles are spherical.

[b] Pt average particle size: Chem = by hydrogen chemisorption, TEM = by TEM analysis.

[c] Difficult to evaluate by TEM, at so low Pt loading.

dehydrogenation reaction. Under the reaction conditions reported in table 1, 0.1 Pt wt% samples of Pt/graphite (Asbury Graphite Mills product, as received) and of Pt/carbon (Carbon Monarch 880, pacified at 900°C with H_2 for 12 h) show at 250°C a specific activity (10^{-4} g MCH/mg Pt) of 19.7 and 49.6 respectively. TEM analysis gives a cluster size distribution average of 15 Å in the samples on graphite and less than 10 Å for the system on carbon monarch, indicating a slightly higher metal dispersion in the latter catalyst. Additional investigations are presently in progress.

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References

[1] K.J. Klabunde, Y.X. Li and B.J. Tan, Chem. Mater. 3 (1991) 30, and references therein.

[2] S.C. Davis, S. Severson and K.J. Klabunde, J. Am. Chem. Soc. 103 (1981) 3024.

[3] M. Dini, Ph.D. Thesis, University of Pisa, Italy (1984);
V. Akhmedov and K.J. Klabunde, J. Mol. Catal. 45 (1988) 193.

[4] P.H. Maitlis, Chem. Soc. Rev. 10 (1981) 1.

[5] G. Vitulli, J. Krauss, P. Salvadori, A. Parmaliana, F. Frusteri and N. Giordano, Congresso Interdivisionale della Societá Chimica Italiana, S. Benedetto del Tronto, September 30–October 5, 1990, Italy, Abstract 581.

[6] A.M. Feltham and M. Spiro, Chem. Rev. 71 (1971) 177, and references therein.
[7] K.J. Klabunde, P. Timms, P.S. Skell and S.D. Ittel, Inorg. Synth. 19 (1979) 59.
[8] L. Leoni, F. Marchetti, G. Sbrana, G. Braca and G. Valentini, Annali di Chimica 69 (1979) 59.
[9] A. Parmaliana, F. Frusteri, A. Mezzapica and N. Giordano, J. Catal. 111 (1988) 235.
[10] M.D. Smolikov, A.S. Belyi, A.I. Nizovskii, I.E. Smirnova, A.S. Semikolenov and V.K. Duplyakin, React. Kinet. Catal. Lett. 37 (1988) 437.