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PRIORITY COMMUNICATION

Outstanding Performances of Magnesia-Supported Platinum–Tin Catalysts for Citral Selective Hydrogenation

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Magnesia-supported Sn–Pt catalysts were prepared by reaction between preformed platinum metal particles and $Sn(n\text{-}C_4H_9)_4$. HRTEM and H_2-chemisorption data confirm the synthesis of very small tin-decorated platinum particles (∼1.0 nm mean diameter). Preliminary studies on catalytic hydrogenation of citral in a trickle-bed reactor reveal that 97% selectivity to unsaturated alcohols at 100% conversion can be easily achieved. The electronic ligand effect produced by the basic support is supposed to be fundamental to enhance the selectivity to unsaturated alcohols and to stabilise the bimetallic particles. © 1999 Academic Press

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INTRODUCTION

The development of heterogeneous catalysts for the selective hydrogenation of α,β-unsaturated aldehydes to the corresponding unsaturated alcohols has attracted much interest for their potential utilisation in the production of valuable intermediates. High selectivities are strongly requested since the conventional stoichiometric processes generally lead to 100% production of unsaturated alcohols.

From the literature data clearly emerges that the Os, Ir, and Pt-based systems show a remarkable selectivity in these reactions (1). To further improve the selectivity to unsaturated alcohols of supported-metal catalysts, the introduction of promoters (IA-IIA elements, transition metals, or s,p-block elements) is necessary. In this respect Pt–Sn and Pt–Ge based catalysts are probably the systems where the best promoting effects are achieved (2). It was, however, reported for different Pt-modified systems that fast ageing processes take place while working in flow conditions (3), thus limiting the working lifetime of catalysts. A pulsed-flow strategy was recently proposed to overcome this problem (4), but even in that case the selectivity to unsaturated alcohols was never better than about 65% at 40–50% conversion.

The challenge is to obtain a highly selective and active catalyst, which also shows a high stability in terms of catalytic performances and which, hopefully, regains the initial properties after an appropriate regeneration process. Our approach to meet these requirements consists of the utilisation of MgO as the support to obtain electron-rich metallic particles. In the case of palladium it is in fact reported that the utilisation of magnesia leads to the formation of very small electron-rich supported metallic particles (5). In this respect it must be pointed out that different authors (1) reported that a shift of electron density from the support to the metal particle should be very limited in the space, and hence no variation should be expected from the catalytic point of view. However, with very small metallic particles, say about 1 nm, electronic effects could play a fundamental role. Since it was recently shown that such very small Pt particles can be synthesised on supports like SiO_2 and hydrotalcite (6), we have decided to develop a novel organometallic-based Pt–Sn/MgO catalyst. It is important to note that the surface organometallic chemistry on metals can be a very clean way to selectively add a second metal at the surface of a first one. By using this approach Claus *et al.* (7) achieved the highest selectivity to date for crotyl alcohol (85% selectivity at 65% conversion) in the gas phase hydrogenation of crotonaldehyde.

In this preliminary communication we will present the outstanding catalytic performances obtained with these new Pt–Sn/MgO catalysts in the selective hydrogenation of citral that was chosen as a model reaction and carried out in a trickle-bed reactor. Flow reaction conditions were adopted to better evaluate stability and regenerability of the catalyst.

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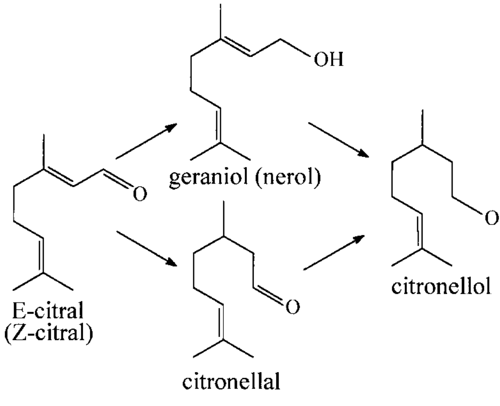
METHODS

Magnesia (Carlo Erba, reagent grade) was refluxed in doubly distilled water for 2 h, heated in air to 773 K, and then evacuated ($p = 10^{-4}$ Pa) overnight at this temperature. This treatment results in magnesia with a surface area of ca. 200 m^2/g, as measured with nitrogen adsorption. Pt–Sn/MgO catalysts were prepared using a two-step procedure. The first step involves a solvent impregnation of $Pt(acac)_2$ on pretreated MgO, which is carried out in toluene at room temperature; after 6 h the sample is vacuum-dried and reduced in the static mode from room temperature to 773 K (heating rate 10 K/min, then hold for 1 h). On this reduced Pt/MgO catalyst $Sn(Bu)_4$ is impregnated in toluene at room temperature for 12 h and then dried under vacuum. The catalyst is then reduced as for $Pt(acac)_2$ on MgO. The Pt loading is 1.0 wt% and the amount of tin is 0.3 wt% (in order to have a Sn/Pt molar ratio of 0.5). A Sn/Pt ratio of 0.5 was chosen after a series of batch tests (carried out at different Sn/Pt values) that have shown a typical volcano profile with the highest selectivities to unsaturated alcohols at Sn/Pt ratios around 0.5–0.6.

Catalytic tests were carried out in a micropilot trickle-bed reactor MCB 890 from Vinci Technologies, with 600 mg of catalyst which are loaded into the reactor (s.s. tube, 100 mm length × 6.35 mm i.d.) and then activated in H_2 flow (100 ml/min, $P = 100$ kPa) at 773 K for 1 h. Optimised catalytic conditions are 373 K, 2 MPa, 100 ml/min of hydrogen flow, 2 μl/min of substrate flow ($\tau = 79.5$ s). A mixture of solvent-free *trans*- and *cis*-citral (3,7-dimethyl-2,6-octadienal; Aldrich C8,300-7) was used as substrate. Total conversion is reported as the percentage of citral consumed. The selectivity to unsaturated alcohols is reported as (moles of unsaturated alcohols)/(total moles of products) × 100, which, according to Scheme 1 means (moles of geraniol + moles of nerol)/(total moles of products) × 100.

Hydrogen chemisorption measurements were obtained in the pulse-mode on a Micromeritics Pulse Chemisorption 2700 apparatus at 373 K. HRTEM micrographs were carried out with a JEOL 2000EX HRTEM. Metal particles distribution versus diameter has been obtained at ×600000 magnification after at least 300 counts.



SCHEME 1

RESULTS AND DISCUSSION

Although an exclusive interaction between Pt and Sn could be obtained by impregnation with a bimetallic precursor like *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$, it was reported that with this procedure the formation of Pt–Sn alloys takes place (8). A two-step preparation procedure was instead adopted to obtain a tin-decorated platinum surface. In fact, as reported for a Pt/SiO_2 catalyst (6), in these conditions the tin precursor interacts selectively with the preformed Pt^0 particles. Even with MgO we have observed that the presence of preformed Pt^0 supported particles is a necessary condition to extract the alkyl-tin precursor from the impregnation solvent.

A coarse evaluation of the influence of reaction parameters on the catalytic performances was carried out in order to establish suitable catalytic conditions. As expected, we found that the conversion increases by increasing the temperature in the range between 323 and 423 K, while the selectivity to unsaturated alcohols decreases: a good compromise was found at 373 K. No sensible variation of the catalytic behaviour was observed as a function of pressure between 2 and 4 MPa (steps of 0.5 MPa, 20 h of time of stream each). Interestingly, both the selectivity to unsaturated alcohols and the total conversion increase by raising contact times (50% conversion and 76% selectivity at $\tau =$ 32 s, 100% conversion and 97% selectivity at $\tau = 79.5$ s).

In Fig. 1 are reported the results of the catalytic hydrogenation of citral carried out with a Pt–Sn/MgO catalyst (Pt 1%, Sn/Pt = 0.5) under optimised conditions. We can observe that the catalyst is not very active at the beginning of the test, but after an induction period of about 10 h the conversion raises steeply to 100%. As can be seen the selectivity to unsaturated alcohols parallels the increase of conversion, starting from an initial value of 90% and reaching 97%. Moreover, after this period no traces of the partially saturated aldehyde (citronellal) were detected, with citronellol being the only by-product (3%).

It is noteworthy that these excellent catalytic performances are representative of a very stable catalytic situation, since no traces of deactivation are observed even after 100 h of testing. In fact, as we have yet discussed, the lifetime and also the regenerability of the catalyst have to be considered as highly valuable features, not easily obtainable with Pt–Sn systems. In our case (see Fig. 2a) more than 90 hours of fast ageing (increased reaction temperature and higher substrate/H_2 ratio) were necessary to observe only a 25% loss of activity. Since it was difficult to further deactivate the catalyst, the effectiveness of a reductive regeneration

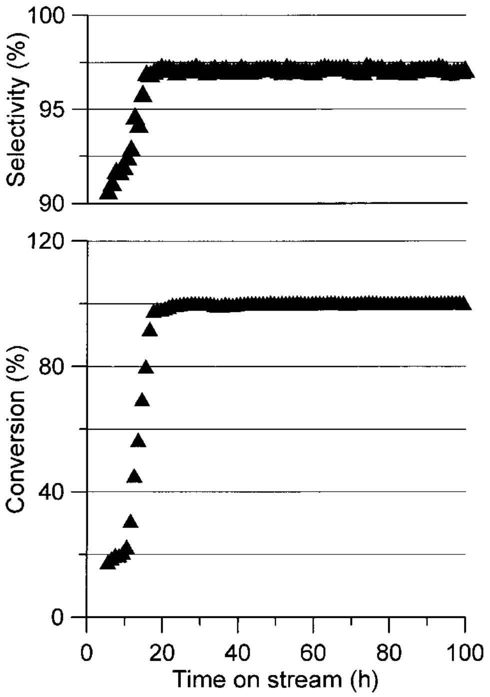


FIG. 1. Hydrogenation of citral on Pt–Sn/MgO (Pt = 1 wt%, Sn/Pt = 0.5). Conversion and selectivity to unsaturated alcohols at 373 K, 2 MPa, 100 ml/min H_2 flow, 2 μl/min substrate flow ($\tau = 79.5$ s).

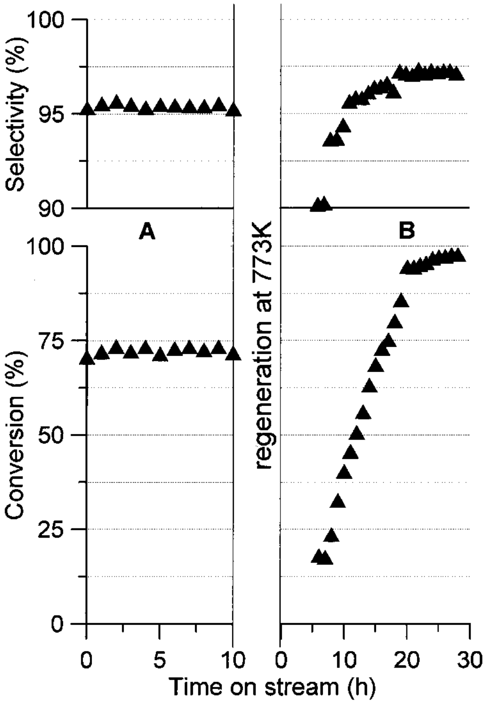


FIG. 2. Catalytic performances recorded using the same catalytic conditions of Fig. 1, after 90 h of fast ageing at 423 K, 2 MPa, 10 ml/min H_2 flow, 20 μl/min substrate flow: (A) after fast ageing; (B) from (A) after 1 h of reduction at 773 K, 100 ml/min H_2 flow, 100 kPa.

procedure was investigated at this point and, as a result, the same catalytic behaviour of the fresh catalyst was restored (compare Fig. 1 with Fig. 2b).

In the same catalytic conditions, very good selectivities were obtained even for the unpromoted Pt/MgO catalyst (70% selectivity to unsaturated alcohols at 100% conversion), which could be a direct proof of the beneficial electronic effects exerted by MgO. Another important difference between Pt–Sn/MgO and Pt/MgO is that with the unpromoted catalyst no induction period is observed.

The presence of an induction period in the selective hydrogenation of α,β-unsaturated aldehydes is quite common with tin promoted catalysts. Generally it has been related to a partial (or total) oxidation of tin, which is necessary to activate the carbonyl hydrogenation (1): during this induction period high activity and hence selectivity toward C=C hydrogenation are commonly observed. In this respect the behaviour of Pt–Sn/MgO is quite uncommon, since the activity of the catalyst is very low at the beginning and the partially saturated aldehyde (citronellal) is always a minor product.

To explain this behaviour it could be suggested that the presence of very small Pt particles, together with the tin decoration, must be fundamental to prevent the presence of extended Pt surfaces. In this way the catalyst could never behave as an unpromoted Pt catalyst and starts to be active only when C=O adsorption is favoured, i.e., when tin oxidation takes place.

To establish the dimensions of Pt and Pt–Sn particles both H_2 chemisorption and HRTEM measurements were carried out. The particle size distributions observed for Pt/MgO and Pt–Sn/MgO, as detected by HRTEM, are reported in Fig. 3. We can observe in both cases a very narrow size distribution, with a very small mean particle diameter. As observed for other Pt–Sn catalysts (9), Pt–Sn/MgO particles are smaller than Pt/MgO ones (0.99 nm against 1.28 nm), which probably means that tin avoids particle sintering during repeated high temperature treatments. The H/Mt values obtained by chemisorption measurements on Pt/MgO and Pt–Sn/MgO are 0.98 and 0.52, respectively. According to the empirical relationship $d_p \cong 1.13/(H/Mt)$ (10) (where d_p is the particle diameter in nm), the particle dimension of the unpromoted catalyst as detected by chemisorption agrees with the HRTEM data. Considering that for the bimetallic system the Sn/Pt ratio is 0.50, the markedly lower H/Mt value observed with Pt–Sn/MgO is consistent with a tin-surface-enriched description. In fact, since the mean particle size decreases passing from Pt to Pt–Sn, we would expect H/Mt values higher than 0.52 for alloy-type particles. This means that, from HRTEM and chemisorption data, the presence of very small tin-decorated platinum particles is strongly suggested.

The particle description previously hypothesised to explain the catalytic behaviour of the Pt–Sn/MgO system is

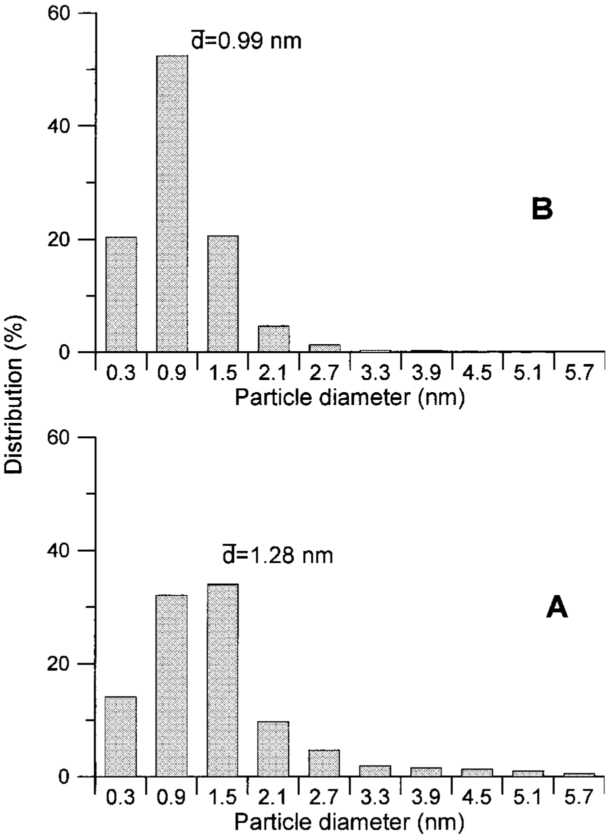


FIG. 3. Particles size distribution of freshly prepared and reduced catalysts: (A) Pt/MgO (Pt = 1 wt%), (B) Pt–Sn/MgO (Pt = 1 wt%, Sn/Pt = 0.5).

thus strengthened by these preliminary results. However, the excellent catalytic performances attained by means of the utilisation of magnesia cannot be ascribed to an ensemble-size effect, since very small particles are obtained even with other supports. Instead, it could be suggested that an electronic ligand effect is produced by the basic support, while the mechanism of an electrophilic activation of the C=O bond could account for the promoting effect of tin.

CONCLUSIONS

This investigation highlights the following points:

(i) Pt–Sn/MgO catalysts prepared in highly dispersed states by surface organometallic chemistry are extremely selective in the citral hydrogenation.

(ii) Comparison with supported Pt–Sn catalysts previously studied shows that the utilisation of magnesia enhances the selectivity to unsaturated alcohols and stabilises the bimetallic particles.

(iii) Preliminary results on catalyst characterisation suggest that the morphology of the bimetallic particles is consistent with the tin-surface-enriched model.

(iv) Up to date Pt–Sn/MgO has to be considered as the heterogeneous catalyst with the best catalytic performances for the citral selective hydrogenation.

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