Characterization and catalytic activity of Al_2O_3-supported Pt–Co catalysts

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A series of Pt–Co supported on γ-alumina have been prepared from acetylacetonate precursors with 2 wt% as total metal loading and different atomic contents. The catalysts were characterized by hydrogen chemisorption, TPR, TEM, XPS and they were tested in two different reactions: methylcyclohexane dehydrogenation and *n*-butane hydrogenolysis. The results have shown that platinum is in reduced state and cobalt is mainly in an oxidized state. Additionally, TEM results evidence an increase in the particle size as cobalt content is increased, in agreement with chemisorption results. Monometallic platinum and cobalt supported catalysts showed large differences in the dehydrogenation of methylcyclohexane, while the bimetallic catalysts have activities in the same order of magnitude with respect to the pure platinum catalyst. In *n*-butane hydrogenolysis all the catalysts show a large decrease in activity compared to other, previously studied Pt-based bimetallic catalysts.

Keywords: catalyst, platinum, cobalt, chemisorption, TPR, XPS, acetylacetonates

1. Introduction

The behaviour of monometallic catalysts may be modified by several ways, among which the addition of a second metal. This addition may have as an effect to limit the number of possible paths to one in selective hydrogenation. For example, Pt_{80}–Fe_{20} catalyst supported by charcoal [1] is known to limit the hydrogenation of cinnamic aldehyde into cinnamic alcohol, which is an important component used in perfume industry. Addition of rhenium to monometallic platinum catalysts supported by alumina is largely used in naphtha reforming to reduce the sintering rate of the platinum particles [2–4]. Some other bimetallic systems, such as Pd–Ni, Pd–Cr or Pd–Cu supported by silica, are also known to be completely selective for the hydrogenation of 1,3-butadiene into butanes [5,6].

However, very few studies have been published on the Pt–Co system, which is known to have high activity in methanol formation at defined compositions [7–9]. These studies have used inorganic precursors for Pt and Co. It is well known that the nature of the metal precursors may influence the activity, selectivity and also the possibility of formation of alloys [10,11]. Even though organometallic compounds are presently starting to be largely used to produce bimetallic catalysts [12,13], they have never been used to obtain Pt–Co/Al_2O_3 catalysts.

The aim of this work is, consequently, to study the preparation and activation of these catalysts and carry out their characterization to obtain some information about their surface properties and their catalytic behaviour in methylcyclohexane dehydrogenation and in *n*-butane hydrogenolysis.

2. Experimental

Catalyst preparation. The Pt–Co catalysts were prepared by impregnation of a γ-alumina (purchased from Rhône-Poulenc, $S_{BET} = 300$ m^2 g^{-1}, porous volume $= 0.39$ cm^3 g^{-1}). The starting materials were metal acetylacetonates obtained from Aldrich. They were dissolved in toluene at room temperature before contacting with alumina. Several concentrations were obtained by varying the relative contents in both metals with 2 wt% as total metal loading. After stirring for 1 h, the toluene excess was eliminated by evaporation and the solids were dried overnight in a stove at 393 K. Then, the catalysts were calcined 2 h under oxygen flow at 573 K and finally reduced 2 h in flowing hydrogen (50 cm^3 min^{-1}) at 773 K. Chemical analysis of Pt and Co in the prepared catalysts shows only small differences (ca. 2%) with respect to the nominal loading. Moreover, all the compositions given in this paper refer to the atomic composition of a bimetallic phase.

TPR experiments. These experiments were carried out from the calcined state in a conventional flow system, fitted with a TCD for monitoring hydrogen con-

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sumption. The reducing gas was a mixture of 5% hydrogen in argon (40 cm^3 min^{-1}) and the heating rate was 6 K min^{-1}.

Hydrogen chemisorption. Adsorption measurements were carried out in a greaseless volumetric system, which uses a MKS instrument as a pressure transducer. Adsorption isotherms were measured at room temperature and irreversible gas uptake was obtained by back extrapolation of the linear part to zero pressure.

TEM experiments. These experiments were performed on a Jeol 1200 equipment operating at 120 kV, with a resolution of 6 Å. All the micrographs were obtained from extractive replica [14].

XPS experiments. XPS spectra were obtained using a Fisons Escalab 200R spectrometer with a hemispherical analyser operating in the constant pass energy mode. A monochromatized Al K_α (1.486,8 keV) radiation operating at 10 mA and 12 kV was used as exciting source. The spectrometer is equipped with a high pressure reaction cell to carry out treatments at high temperatures. The catalysts were pressed on a copper grid to form thin samples and placed in the high pressure cell. Afterwards, the samples were reduced in flowing hydrogen at 773 K for 2 h. They were transported into the analysis chamber without contacting air. The C 1s line at the binding energy of 282.9 eV was used as an internal standard. The intensity of the XPS peaks was obtained using S-shape background subtraction and integration of peaks areas. The Pt/Al and Co/Al atomic surface ratios were estimated from the integrated intensities from the Pt $4d_{5/2}$, Co $2p_{3/2}$ and Al 2p lines using the sensitivity factors of Wagner et al. [15].

Catalytic activity. Catalytic activities for methylcyclohexane dehydrogenation and *n*-butane hydrogenolysis were measured in a fixed-bed microcatalytic reactor working at atmospheric pressure. For the methylcyclohexane dehydrogenation a mixture of H_2/MCHa (16 : 1) was fed into the reactor at a flow rate of 30 cm^3 min^{-1} and for *n*-butane hydrogenolysis a mixture of H_2/*n*-butane (8 : 1) at a flow rate of 50 cm^3 min^{-1} was used. In each experiment 20 mg of catalyst were used. The analyses of reactants and products were carried out with an online gas chromatograph.

3. Results and discussion

In fig. 1 TPR profiles for the Pt–Co/Al_2O_3 catalysts are shown. The reduced samples were previously calcined in air at 673 K for 2 h. For the Pt_{100} samples there are two well defined peaks centered at 380 and 600 K indicating the presence of different types of metal–support interactions [16]. The monometallic cobalt catalyst shows a partial reduction at about 920 K in agreement with previously reported results [17]. This behaviour has been attributed to a strong interaction of cobalt with alumina allowing the formation of spinel-type oxide

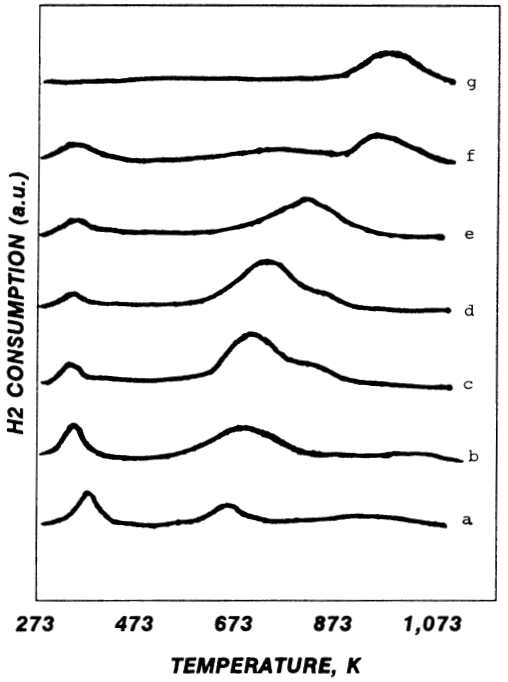

Fig. 1. Temperature reduction profiles of various Pt–Co/Al_2O_3 catalysts: (a) Pt_{100}; (b) $Pt_{90}Co_{10}$; (c) $Pt_{70}Co_{30}$;(d) $Pt_{50}Co_{50}$; (e) $Pt_{30}Co_{70}$; (f) $Pt_{10}Co_{90}$; (g) Co_{100}.

$CoAl_2O_4$ which requires temperatures higher than 1300 K to be reduced.

With respect to bimetallic Pt–Co catalysts the behaviour is similar. We observe a single peak centered at about 330 K which decreases with platinum loading. A second peak centered at about 600 K is also observed. This peak shifts towards higher temperatures as cobalt loading increases, the H_2 consumption being also higher, probably due to a partial reduction of some cobalt oxide species, in agreement with XPS results, as it will be discussed hereafter.

Hydrogen chemisorption results are summarized in fig. 2, in which two different representations have been used. In the first one the hydrogen uptake is expressed as a function of the total amount of metal atoms, while in the second only Pt atoms have been considered. Different behaviours can be seen depending on the variable considered. If the uptake is referred to total metal loading, the amount of chemisorbed hydrogen remains nearly constant up to 30 at% Co and then it decreases drastically with increasing Co content. When hydrogen uptake is referred only to platinum, an approximately constant value is noticed with the exception of the catalyst $Pt_{70}Co_{30}$, for which a raise of about 30% is observed. Taking into account the TPR results it seems more likely that hydrogen is essentially adsorbed on Pt , because of the slight reduction of cobalt. This implies that a reduction of the Pt particle size may occur, associated to an increase in the cobalt content.

Figs. 3a and 3b show the micrographs of two of the studied catalysts. For Pt/Al_2O_3 particles of 1.5–4.0 nm

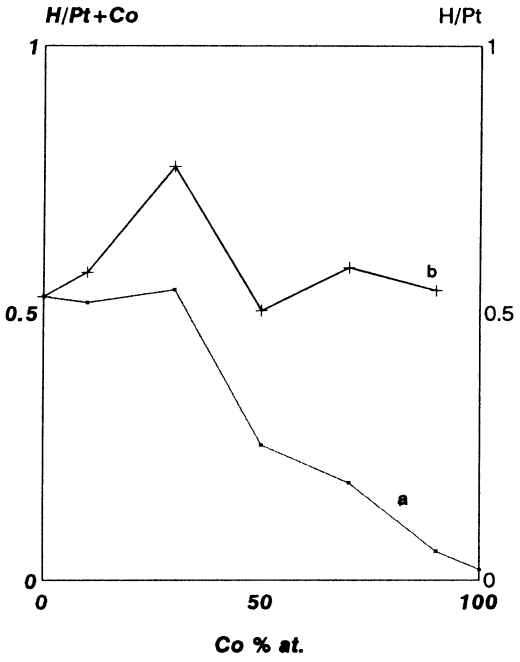

Fig. 2. Hydrogen chemisorption on Pt–Co/Al_2O_3 catalysts. (a) H/(Pt + Co) and (b) H/Pt atomic ratios.

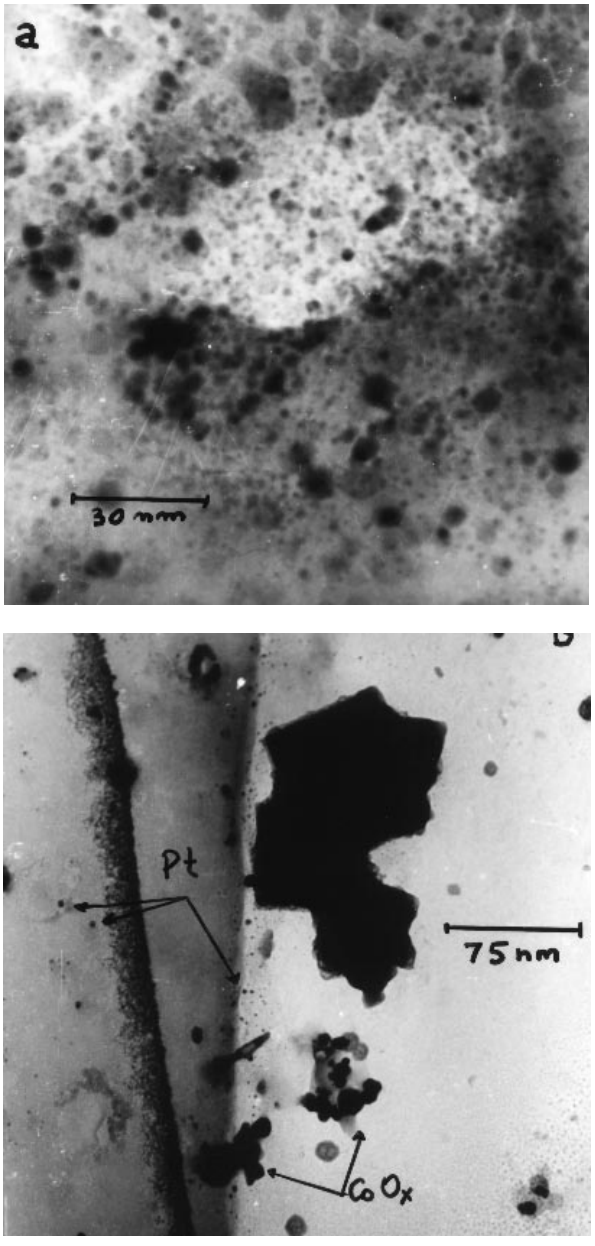

Fig. 3. TEM micrographs of Pt–Co/Al_2O_3 catalysts. (a) Pt_{100}; (b) $Pt_{10}Co_{90}$.

can be observed, the average particle size for this catalyst being about 2.5 nm. When cobalt loading increases, and consequently platinum loading decreases, two different effects can be observed. On the one hand, the platinum particle size decreases, while the cobalt particle size, which presents higher particle size, increases slightly. In fig. 3b it can be seen that cobalt particles are about 15 nm. They correspond mainly to cobalt oxide particles, as shown from XPS results. The observed TEM results are also in line with hydrogen chemisorption, previously discussed.

Table 1 displays binding energies for Pt and Co, surface atomic ratios Pt/Al and Co/Al, and the estimated degree of reduction of cobalt for the series of Pt–Co/alumina catalysts. It can be observed that Pt $4d_{5/2}$ binding energies are very close to the corresponding one for the pure platinum catalyst and are rather randomly distributed around that of pure platinum. Consequently, it cannot be asserted that platinum may be alloyed to cobalt to give bimetallic particles. Conversely, it can be noticed that all the values of the Co $2p_{3/2}$ binding energies in bimetallic catalysts are lowered from 0.3 to 0.8 eV with respect to the value measured in the pure cobalt catalyst. The observed values show that Co is mainly in an oxidized state. A careful decomposition of the experimental peaks allows estimation of the contribution of reduced cobalt, which varies from 19% for the catalyst Pt_{90}–Co_{10} to 7% in the catalyst containing only cobalt. This observation was expected considering the role of noble metals to promote the reduction of the second metal [18].

XPS results reveal an increase in the Pt/Al ratio with increasing cobalt content, reaching a maximum for the catalyst with $Pt_{30}Co_{70}$ and then decreases. This may be explained by considering the change of platinum particle size, and therefore an increasing amount of platinum atoms may be detected by XPS. The decrease of the ratio observed at low platinum concentrations is related with the decrease in the total platinum content with respect to cobalt. The change in the value of the Co/Al surface ratio is due to different factors. On the one hand, metal cobalt particles cover only a small fraction of the surface with thin layers of cobalt oxide particles. As the cobalt loading increases, a parallel increase in the surface coverage and the thickness of the cobalt oxide layers may be produced. On the other hand, because of the different behaviour of cobalt compared to platinum with respect to X-ray absorption, a higher thickness can be detected

Table 1
Binding energies of Pt, Co and Pt/Al and Co/Al surface ratios for Pt–Co/Al_2O_3 catalysts

Catalyst (at%)		Binding energy (eV)		Atomic surface ratio		Reduction degree
Pt	Co	Pt $4d_{5/2}$	Co $2p_{3/2}$	$(Pt/Al)_s \times 10^3$	$(Co/Al)_s \times 10^3$	Co (%)
100	0	315.7	–	1.01	–	–
90	10	315.4	781.4	1.18	0.97	19
70	30	315.8	781.2	1.19	24.54	16
50	50	315.2	781.4	1.45	7.82	17
30	70	315.7	781.7	1.55	8.80	10
10	90	315.3	781.7	0.95	16.37	10
0	100	–	782.0	–	11.39	7

in cobalt particles. This explains the higher Co/Al surface ratio compared with the bulk ratio.

According to the XPS characterization of the samples there is no evidence of formation of Pt–Co alloys, as it has been previously proposed by Zsoldos and Guczi [9]. The main difference with respect to this paper is the nature of precursors. They used a coimpregnation of alumina with cationic and anionic precursors such as H_2PtCl_6 and $Co(NO_3)_2$. In the present paper $Pt(acac)_2$ and $Co(acac)_2$ were used. In this case a competition for the adsorption sites may occur [19] making more difficult the interaction between both metals to produce bimetallic phases.

The catalysts were used in the dehydrogenation of methylcyclohexane, classified as a structure-insensitive reaction [20,21]. Catalytic experiments were run under differential conditions, to avoid mass and heat transfer limitations, for 2 h on stream. Toluene and benzene were the observed products and no deactivation was detected under these conditions. In table 2 the main results are summarized. It can be seen that the turnover number (TON) remains almost constant in all the series of catalysts with the exception of $Pt_{10}Co_{90}$, which presents a higher value, and Co_{100}, which is not active in this reaction. On the other hand, *n*-butane hydrogenolysis presents TON values ranging from 0.005 to 0.01 in the composition range Pt_{100} to $Pt_{70}Co_{30}$; they increase largely for catalysts with higher cobalt content.

Table 2
Catalytic activity expressed as turnover number in methylcyclohexane dehydrogenation and *n*-butane hydrogenolysis on Pt–Co/Al_2O_3 catalysts

Catalyst (at%)		TON (s^{-1})	
Pt	Co	[a]	[b] $\times 10^3$
100	0	0.143	9.3
90	10	0.149	4.9
70	30	0.149	6.2
50	50	0.214	9.6
30	70	0.158	10.5
10	90	0.347	24.5
0	100	not active	46.0

[a] Dehydrogenation of methylcyclohexane at $T = 523$ K.
[b] Hydrogenolysis of *n*-butane at $T = 533$ K.

The activity pattern exhibited by the catalysts may be clearly related to the H/Pt ratio, indicating that the reaction mainly occurs on the platinum surface. The activity of all catalysts in the hydrogenolysis of *n*-butane was very low compared with other metallic catalysts under comparable conditions [22,23]. However, at higher cobalt contents a significant increase in the TON occurs. A similar behaviour has been found for Pd–Co/SiO_2 catalysts, in which cobalt predominantly promotes hydrogenolysis of hydrocarbons [24].

4. Conclusions

The results obtained suggest that the nature of the metal precursor affects strongly the Pt–Co interactions. In this study no evidence of formation of alloy was found using organometallic precursors, meanwhile, with a cationic and an anionic precursor of cobalt and platinum respectively, the formation of Pt–Co alloys has been reported.

TPR and XPS results indicate that platinum promotes a partial reduction of cobalt shifting significantly its reduction peaks. The extent of reduction is very low and it increases slightly with Pt content. Thus, cobalt is mainly in an oxidized state, whereas platinum is in a near-zero valent state.

The catalytic activity in methylcyclohexane dehydrogenation is attributed essentially to platinum particles. Conversely, in the *n*-butane hydrogenolysis an important effect of cobalt was observed.

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