FTIR and XPS study of supported PtSn catalysts used for light paraffins dehydrogenation

Sergio de Miguel, Alberto Castro, Osvaldo Scelza

Instituto de Investigaciones en Catálisis y Petroquímica – INCAPE (Facultad de Ingenieria Quimica, Universidad Nacional del Litoral – CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

José Luis García Fierro and Javier Soria

Instituto de Catálisis y Petróleoquímica, Campus Universidad Autónoma, Cantoblanco, 28049 Madrid, Spain

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A comparison between the characteristics of the metallic phase (studied by FTIR and XPS) of Pt and PtSn catalysts supported on Al_2O_3, K-doped Al_2O_3 and MgO (used for light paraffins dehydrogenation reactions) is reported in this paper. The beneficial effects produced by tin addition to platinum, both in the increase of the selectivity to propene and the low coke formation, would be related with the possible electronic modifications of Pt by Sn, with probable formation of alloys, mainly for Al_2O_3 and MgO supported bimetallic catalysts. On the other hand, the modification of the electronic state of Pt by Sn addition appears to be of a minor importance in bimetallic catalysts supported on K-doped Al_2O_3.

Keywords: metal catalysts; paraffins dehydrogenation; catalyst characterization

1. Introduction

The selective dehydrogenation of light paraffins can be carried out on bimetallic catalysts composed of a noble metal, mainly Pt, and an inactive metal (such as Sn, Ge or Pb). These catalysts exhibit a high hydrogenation–dehydrogenation activity and a relatively low hydrogenolytic capacity. The supports frequently used for these catalysts are acidic oxides (e.g. Al_2O_3, SiO_2–Al_2O_3), which lead both to a high dispersion and stability of the metallic phase. However, these acidic supports can catalyze undesired lateral reactions (cracking and polymerization). For this reason, an increasing number of papers have been recently published on the use of acidic supports modified by alkali metals [1–3] and, even more recently, on the use of basic oxides, mainly alkaline earth oxides [4–7]. Several papers on Pt supported on basic oxide catalysts have been reported in the literature. Thus, a disagreement between the amount of chemisorbed hydrogen and the particle size (measured by TEM) has been found, which is attributed to a strong metal–support interaction in this catalytic system [5–7]. Moreover, the H_2 reduction at different temperatures appears to produce a very important modification of the characteristics of the metallic phase. Evidence on the Pt redispersion after a thermal treatment under oxygen atmosphere has also been reported in the literature [7]. However, there is no information about the surface characteristics of bimetallic catalysts supported on MgO and their behavior in the dehydrogenation of paraffins. From this reason, a comparison between the characteristics of the metallic phase of Pt and PtSn catalysts supported on Al_2O_3, K-doped Al_2O_3 and MgO is reported in this paper. The surface characterization of the metallic function was carried out by using FTIR and XPS. Besides, the catalysts were tested in the propane dehydrogenation reaction to obtain information about the modification of the nature of Pt by tin addition.

2. Experimental

Three different supports were used: a commercial γ-Al_2O_3 CK-300 from Cyanamid Ketjen ($S_{BET} = 190\,m^2\,g^{-1}$), K (1.69 wt%)–$Al_2O_3$ ($S_{BET} = 179\,m^2\,g^{-1}$) obtained by impregnation of γ-Al_2O_3 with an aqueous solution of KOH, and a commercial ultrapure MgO ($S_{BET} = 60\,m^2\,g^{-1}$). Both pure γ-Al_2O_3 and MgO were previously calcined in air at 923 K during 3 h. The K-doped Al_2O_3 support was dried at 393 K during 12 h, and then calcined in air at 773 K.

Bimetallic Pt (0.4 wt%)–Sn (0.4 wt%) supported catalysts were prepared by two different impregnation procedures. The first one consisted in a successive impregnation (denoted as SI). In this case the different supports were impregnated with a hydrochloric solution of $SnCl_2$ (0.024 M), then dried at 393 K and finally impregnated with an aqueous solution of H_2PtCl_6 (0.015 M). The second procedure was a coimpregnation (denoted as C) of the support with a hydrochloric solution (1 M) containing both metallic precursors ($H_2PtCl_6 + SnCl_2$). It must be noted that the HCl addition to the impregnating solution was carried out in order to produce the $SnCl_2$ solution. However, this acid has secondary effects: (i) it acts as a competitor of the Pt precursor adsorption, and (ii) HCl produces a dissolution of small quantities of Al_2O_3 [8]. Monometallic Pt (0.4 wt%) and Sn (0.4 wt%) catalysts supported on Al_2O_3, K-doped Al_2O_3 and MgO were also prepared. Impregnations were carried out at 298 K and the volume of the impregnating solution was 1.4 ml g^{-1} support. After drying at 393 K, samples were calcined in an air stream at 773 K.

The physical properties of γ-Al_2O_3, K-doped Al_2O_3 and MgO (previously evacuated at 773 K for 15 h) were determined in a Micromeritics ASAP 2000 volumetric equipment.

FTIR spectra were taken on a Nicolet 5ZDX spectrometer. All the samples, in the form of compressed self-supporting disks (25 mg cm^{-2}), were previously reduced in H_2 at 853 K and evacuated (under a residual pressure of 10^{-5} Torr) at 723 K during 50 min. Spectra were recorded after adsorbing 30 Torr of CO at 298 K. The background spectrum corresponding to CO gas and the cell windows was subtracted in all cases. In order to determine the spectra at low CO coverages, samples were submitted to successive outgassing treatments (10^{-5} Torr) at increasing temperatures (up to 600 K) until the total disappearance of the linear Pt–CO band. The CO coverages (θ_{CO}) were calculated as the ratio between the integrated area of the linear Pt–CO band after evacuation at a given temperature and that corresponding to the CO adsorption at 298 K without further evacuation.

X-ray photoelectron spectroscopy (XPS) spectra were taken on a Fisions Escalab 200 R spectrometer. Catalysts were previously submitted to several outgassing–H_2 reduction steps at 853 K in the pretreatment chamber.

Catalysts were tested in n-propane dehydrogenation reaction at 853 K in a differential reactor, using a space velocity of 0.067 mol C_3H_8 h^{-1} g cat.$^{-1}$, a sample weight of 200 mg, and a He/C_3H_8 molar ratio = 9. Reaction products were analyzed by gas chromatography, using a column packed with Porapak QS. The accuracies of the mass balances obtained in each chromatographic determination were higher than 99%. Previously, the calcined samples were reduced in H_2 at 853 K. After reaction, the content of coke deposited on the catalysts was determined by micrograviinetric measurements in a Cahn Electrobalance during a temperature programmed oxidation treatment up to 1073 K.

3. Results and discussion

Fig. 1 represents FTIR spectra of CO adsorbed ($\theta_{CO} = 1$) on Pt/Al_2O_3 and $PtSn/Al_2O_3$ catalysts (prepared by different impregnation procedures). The IR spectrum of Pt/Al_2O_3 shows three bands: one at 2203 cm^{-1}, which is characteristic of CO molecules coordinated with tetrahedral Lewis Al^{3+} sites of the alumina surface [9], a second band at 2075 cm^{-1}, which corresponds to the linear form of CO adsorption on Pt particles, and a small band at 1827 cm^{-1}, which is assigned to CO adsorbed in bridge form on two-fold hollow sites of Pt [10]. The band corresponding to CO adsorbed on the Lewis acid sites of the γ-Al_2O_3 was easily removed by evacuation at room temperature due to the weak adsorption of CO on these sites. IR spectra of both bimetallic catalysts supported on Al_2O_3 display the CO–Al^{3+} band at the same frequency as that of the monometallic sample. The band corresponding to the linear Pt–CO is shifted to higher frequencies (2083 cm^{-1}), while the bridged species dissappear in the bimetallic catalysts.

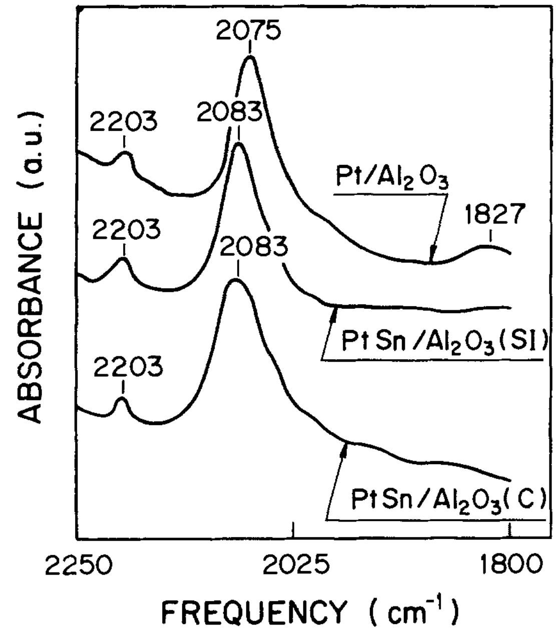

Fig. 1. FTIR of CO adsorbed (P_{CO} = 30 Torr) on Pt/Al_2O_3, $PtSn/Al_2O_3$ (SI) and $PtSn/Al_2O_3$ (C). Catalysts were previously reduced in H_2 at 853 K.

FTIR spectra of CO adsorbed ($\theta_{CO} = 1$) on mono and bimetallic catalysts supported on K-doped Al_2O_3 are shown in fig. 2. The spectrum of the Pt/K–Al_2O_3 sample displays a very small band at 2195 cm^{-1} corresponding to CO adsorbed on the Lewis acid sites of the alumina, a broad band with the maximum at 2063–2073 cm^{-1} in the zone corresponding to the Pt–CO linear adsorption, and two very small bands at 1985 and 1938 cm^{-1}. It must be noted that no bridge-bonded CO species were observed in this sample. By comparing IR spectra of Pt/Al_2O_3 (fig. 1) and Pt/K–Al_2O_3 (fig. 2), it can be observed that the intensity of the IR band due to CO–Al^{3+} interaction decreases and its position shifts from 2203 to 2195 cm^{-1}, after K addition. These effects can be due to a blocking action of K on the tetrahedral Al^{3+} sites [9]. In this sense, it must be indicated that the K addition to Al_2O_3 decreases the total acidity (from

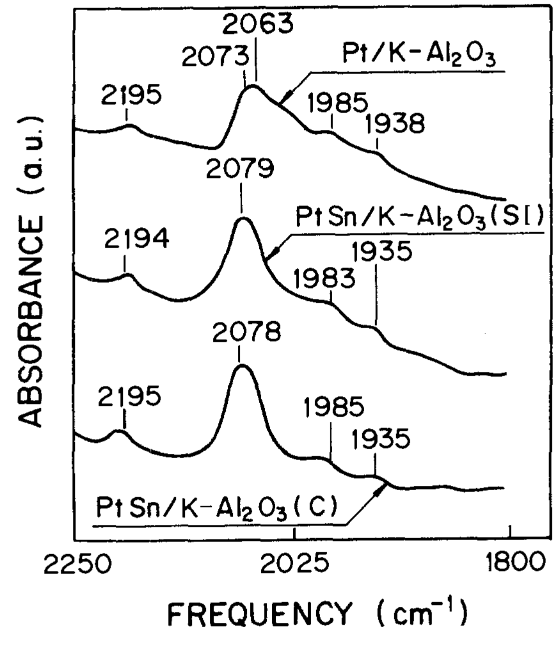

Fig. 2. FTIR of CO adsorbed (P_{CO} = 30 Torr) on Pt/K–Al_2O_3, PtSn/K–Al_2O_3 (SI) and PtSn/K–Al_2O_3 (C). Catalysts were previously reduced in H_2 at 853 K.

0.404 for Al_2O_3 to 0.148 meq NH_3 g^{-1} for K(1.67 wt%)–Al_2O_3). This diminution is mainly due to the poisoning effect of K on the stronger acid sites [11]. On the other hand, IR spectra of both PtSn/K–Al_2O_3 catalysts are very similar to that of Pt/K–Al_2O_3 sample, except that the linear Pt–CO band is shifted towards higher frequencies (2078 and 2079 cm^{-1}).

Fig. 3 shows FTIR spectra of CO adsorbed ($\theta_{CO} = 1$) on Pt/MgO and PtSn/MgO catalysts. The monometallic catalyst displays two peaks (2075 and 2088 cm^{-1}), characteristic of CO adsorbed in linear forms. Spectra of both PtSn/MgO catalysts are very similar and display only one band at 2074–2075 cm^{-1}. No bridge Pt_2CO species were observed in both mono and bimetallic samples.

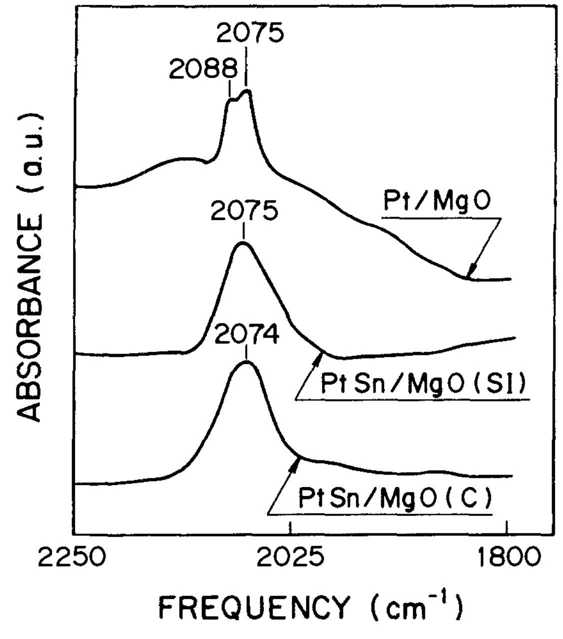

Fig. 3. FTIR of CO adsorbed (P_{CO} = 30 Torr) on Pt/MgO, PtSn/MgO (SI) and PtSn/MgO (C). Catalysts were previously reduced in H_2 at 853 K.

At high CO coverages, the platinum surface is covered by a monolayer of CO molecules ($\theta_{CO} = 1$). In these conditions, in addition to electronic factors, the frequencies of the absorption bands may be affected by the dipole–dipole interaction of the adsorbed CO molecules. In order to minimize this dipole–dipole effect, and hence to obtain more accurate information about the electronic state of Pt centers, we carried out additional FTIR experiments. Thus, samples previously saturated with CO ($\theta_{CO} = 1$) were submitted to successive outgassing treatments at 10^{-5} Torr and increasing temperatures (up to 600 K) until the total disappearance of the linear Pt–CO band. In a previous paper, Primet [12] found, by using isotopic dilution techniques with mixtures of ^{12}CO and ^{13}CO, that the frequency of the linear Pt–CO band extrapolated at infinite dilution of ^{12}CO was equal to the frequency limit obtained after the thermal desorption of CO. We observed for all the catalysts that the Pt–CO frequency decreased continuously when the CO coverage diminished. The extrapolation of this curve to $\theta_{CO} = 0$ would give the frequency of the isolated CO molecule (singleton frequency), since the dipole–dipole interaction is suppressed. Table 1 shows the frequency values of the linear Pt–CO band obtained for the different mono and bimetallic catalysts, both at $\theta_{CO} = 1$ and at $\theta_{CO} = 0$ (singleton frequency). The frequency of the linear Pt–CO species is equal to 2075 cm^{-1} (at $\theta_{CO} = 1$) for Pt/Al_2O_3 sample. The progressive desorption of adsorbed CO shifts the frequency to 2051 cm^{-1}. This singleton frequency value is very close to 2052 cm^{-1}, the value reported by Primet [12] for a Pt/Al_2O_3 catalyst. On the other hand, PtSn/Al_2O_3 catalysts show lower singleton frequencies (2045–2046 cm^{-1}) than that corresponding to the Pt/Al_2O_3 sample (2051 cm^{-1}). This shift of the IR band corresponding to the isolated CO molecule could be due to an electronic modification of the Pt

Table 1

Frequency values of the linear Pt–CO IR band for the different mono and bimetallic catalysts at $\theta_{CO} = 1$ (total CO coverage) and at $\theta_{CO} = 0$ (singleton frequency)

Catalyst	Freq. at $\theta_{CO} = 1$ (cm^{-1})	Freq. at $\theta_{CO} = 0$ (cm^{-1})
Pt/Al_2O_3	2075	2051
PtSn/Al_2O_3 (SI)	2083	2046
PtSn/Al_2O_3 (C)	2083	2045
Pt/K–Al_2O_3	2063–2073	2034
PtSn/K–Al_2O_3 (SI)	2079	2039
PtSn/K–Al_2O_3 (C)	2078	2038
Pt/MgO	2075–2088	2051
PtSn/MgO (SI)	2075	2041
PtSn/MgO (C)	2074	2040

centers by tin addition. This effect is more pronounced in bimetallic catalysts supported on MgO, since the singleton frequencies (2040–2041 cm^{-1}) of both PtSn/MgO samples are much lower than that corresponding to the monometallic Pt/MgO catalyst (2051 cm^{-1}). On the other hand, the singleton frequencies in PtSn/K–Al_2O_3 catalysts appear at 2038–2039 cm^{-1}, much lower than that corresponding to the Pt/Al_2O_3 sample, but very close to that of the Pt/K–Al_2O_3 catalyst (2034 cm^{-1}). Consequently, in bimetallic catalysts supported on K-doped Al_2O_3, it seems that the electronic state of Pt is strongly affected by K addition, while tin addition to Pt/K–Al_2O_3 only produces a slight modification of the singleton frequency. Hence, the effect of tin addition to Pt supported on K-doped Al_2O_3 is difficult to explain only by FTIR measurements.

XPS spectra of Pt $3d_{5/2}$ and Sn $3d_{5/2}$ levels for the different bimetallic catalysts after reduction at 853 K are shown in figs. 4 and 5, respectively. It must be indicated that the Pt 4f lines were difficult to analyze because these lines were overlapped by the Al 2p lines. The binding energy values of the different peaks for mono and bimetallic catalysts are shown in table 2. The Pt $3d_{5/2}$ and Sn $3d_{5/2}$ binding energies for the bimetallic catalyst supported on a given support were not modified by using different impregnation procedures (successive impregnation or coimpregnation). Hence, only XPS results corresponding to bimetallic catalysts prepared by successive impregnations (SI) are reported in table 2 and figs. 4 and 5. Bimetallic samples supported on Al_2O_3, K-doped Al_2O_3 and MgO show slightly higher Pt $3d_{5/2}$ binding energy values with respect to those of the corresponding monometallic samples supported on each support. This shift could be due to an electronic modification of the Pt centers by tin addition.

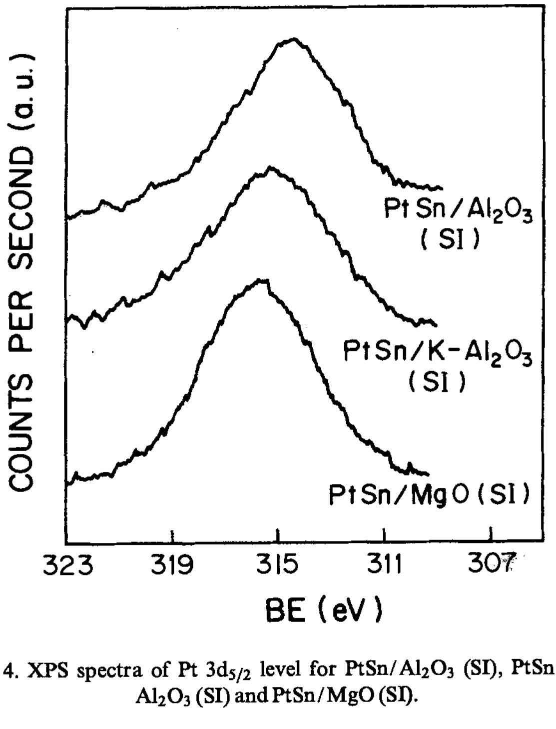

Fig. 4. XPS spectra of Pt $3d_{5/2}$ level for PtSn/Al_2O_3 (SI), PtSn/K–Al_2O_3 (SI) and PtSn/MgO (SI).

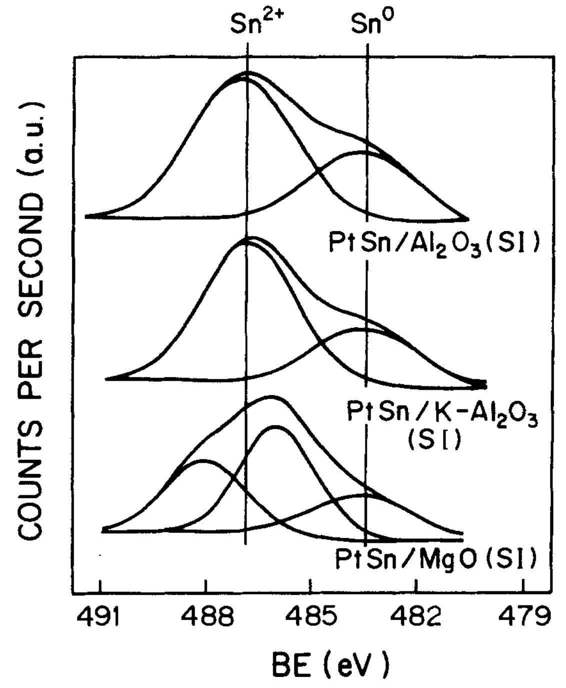

Fig. 5. XPS spectra of Sn $3d_{5/2}$ level for PtSn/Al_2O_3 (SI), PtSn/K–Al_2O_3 (SI) and PtSn/MgO (SI).

From the deconvolution of the XPS spectra of the Sn $3d_{5/2}$ level for bimetallic PtSn samples supported on Al_2O_3 and K-doped Al_2O_3 (fig. 2), two peaks were obtained: one at 483.5–483.7 eV due to metallic tin (zerovalent Sn), and the other one at approximately 486.7–487.0 eV corresponding to Sn(II,IV) species. On the other hand, the deconvolution of the Sn $3d_{5/2}$ level for the PtSn/MgO catalyst shows the presence of three peaks: the first at 483.7 eV corresponding to Sn(0), a second one at 486.0 eV due to Sn(II, IV) species, and a third one at 488.0 eV, probably due to oxidized tin species stabilized on the MgO support. Besides, table 2 shows the surface ratios between the zerovalent Sn and the total Sn (Sn_0/Sn_T), and between the total Sn and the total Pt (Sn_T/Pt_T). All bimetallic catalysts display a similar percentage of Sn_0 (between 24 and 33%). Additional XPS experiments on monometallic Sn catalysts supported on

Table 2
XPS results, binding energies of the Pt $3d_{5/2}$ level, surface atomic ratios Sn_0/Sn_{total} (obtained from deconvolution of XPS spectra of the Sn $3d_{5/2}$ level) and surface ratio Sn_T/Pt_T

Catalyst	BE Pt $3d_{5/2}$ (eV)	Sn_0/Sn_T	Sn_T/Pt_T
Pt/Al_2O_3	314.2	–	–
PtSn/Al_2O_3 (SI)	314.7	0.33	3.0
Pt/K–Al_2O_3	315.0	–	–
PtSn/K–Al_2O_3 (SI)	315.1	0.32	2.5
Pt/MgO	315.5	–	–
PtSn/MgO (SI)	315.8	0.24	2.0

the different supports and submitted to similar reduction treatments only showed Sn(II, IV) surface species. These results are in agreement with previous XPS measurements which indicate that a fraction of the tin in the reduced $PtSn/Al_2O_3$ is present in the zerovalent state and probably alloyed with Pt(0) [13–15]. Moreover, Srinivasan and Davis [16] found PtSn alloys with a composition of PtSn (1 : 1) by using an in situ XRD technique, both for $PtSn/Al_2O_3$ samples with low and high metal loading. Besides, several authors found different PtSn alloys in reduced $PtSn/Al_2O_3$ catalysts of low metal loading, by using Mössbauer spectroscopy [17–19]. Furthermore, the high values of the Sn_T/Pt_T surface ratios (table 2) in bimetallic catalysts supported on Al_2O_3 and K-doped Al_2O_3, compared with the value of the Sn_T/Pt_T bulk ratio (equal to 1.6), indicate an important Sn surface enrichment in these catalysts. However, this effect seems to be lower in bimetallic samples supported on MgO.

Fig. 6 shows the selectivity to the different products in the propane dehydrogenation reaction carried out in a differential flow reactor at 853 K. Two kinds of reaction products were obtained: (a) propene (from propane dehydrogenation), (b) methane, ethane and ethene (from propane cracking and hydrogenolysis). In all cases, no aromatic hydrocarbon was detected.

It can be observed that the selectivity to propene is enhanced in all the bimetallic catalysts, mainly in those supported on MgO (fig. 6). In this case, the dehydrogenation selectivity increases from 46% for Pt/MgO to 90% for the coimpregnated PtSn/MgO. Similar results were found by Barias et al. [20], who reported that the selectivity to propene over $PtSn/Al_2O_3$ and $PtSn/SiO_2$ samples were higher than those corresponding to the monometallic catalysts. Nevertheless, there is no information about dehydrogenation of paraffins on bimetallic catalysts supported on MgO.

Other important beneficial effect of these bimetallic catalysts is the low coke formation, as shown in fig. 7, mainly in PtSn/MgO samples, where a negligible coke formation (after 2 h of reaction at 853 K) was detected. In a recent paper, Szanyi et al. [21] found, after *n*-butane hydrogenolysis at 575 K, negligible carbonaceous deposits on two different Sn/Pt(111) surface alloys, while a significant carbon level was detected on the surface of the Pt(111) catalyst. From the above mentioned evidence and our results, it can be assumed that coke formation would be inhibited by the presence of significant amounts of PtSn alloys in PtSn catalysts supported on Al_2O_3 and on MgO. Surprisingly, both mono and bimetallic catalysts supported on K-doped Al_2O_3 also show a very low amount of coke after reaction. The reasons for the inhibition of the coking capacity of Pt/Al_2O_3 by K addition were extensively explained in a previous paper [22]. In monometallic $Pt/K–Al_2O_3$ catalysts, electronic effects of K on Pt could be produced through modifications of the support properties, which induce a change in the metal–support interaction. In fact, Lewis Al^{3+} sites are blocked by K ions and the support properties would change from acidic to more basic ones, leading to an electron transfer from the modified support to Pt. This effect could produce a lower adsorption strength of the coke precursors on the metallic surface, leading to a low amount of coke on the metal. Moreover, the poisoning effect of K on the acid sites of the alumina surface also produces the inhibition of the polymerization reactions of the dehydrogenated products to coke precursors.

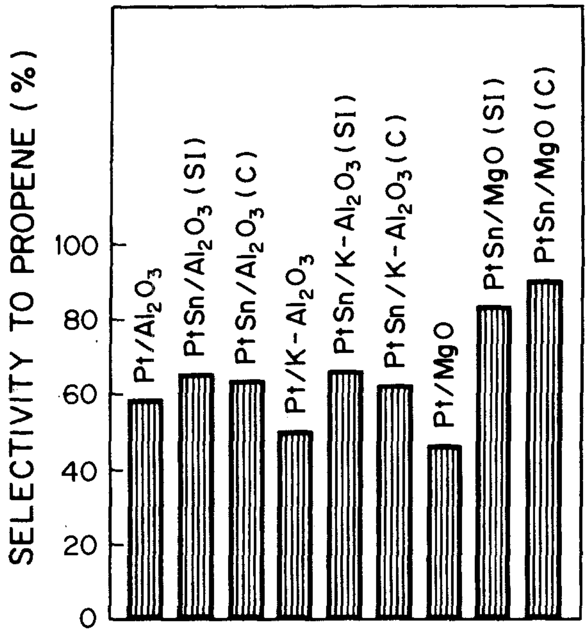

Fig. 6. Selectivities to propene (during propane dehydrogenation at 853 K) for mono and bimetallic catalysts.

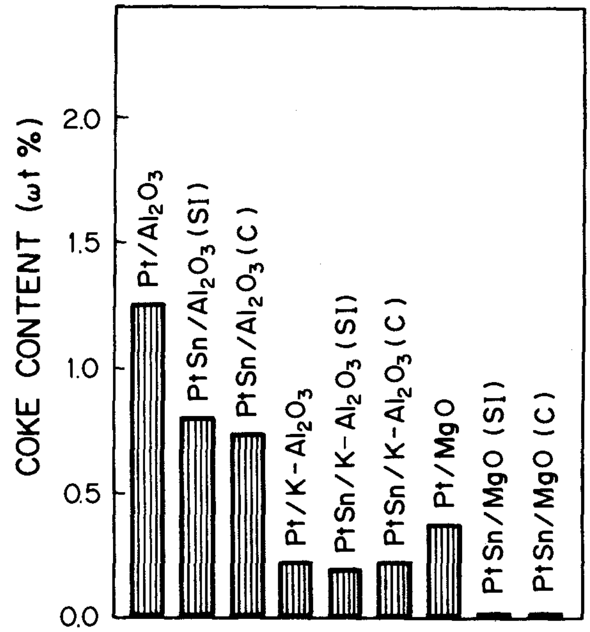

Fig. 7. Coke formation on different mono and bimetallic catalysts after 2 h of propane dehydrogenation at 853 K.

XPS results clearly indicate that in PtSn catalysts supported on Al_2O_3 and MgO an important portion of Sn is in zerovalent state. Moreover, both the shift of the Pt $3d_{5/2}$ binding energy and the decrease of the linear Pt–CO singleton frequencies (in FTIR experiments) after tin addition for these bimetallic catalysts supported on Al_2O_3 and MgO are important evidences of the existence of important electronic modifications of Pt by Sn addition, with a probable formation of intermetallic alloys.

On the other hand, in PtSn/K–Al_2O_3 catalysts, though an important fraction of tin was found in zerovalent state after reduction, results of FTIR, XPS and the low amounts of coke deposited after reaction showed a slight modification of the Pt centers by tin addition. Hence, the modification of the electronic state of Pt by Sn addition appears to be of a minor importance in these catalysts.

In conclusion, the beneficial effects produced by tin addition to platinum, both in the increase of the selectivity to propene and the low coke formation, would be related with the possible electronic modifications of Pt by Sn, mainly for Al_2O_3 and MgO supported bimetallic catalysts. This modification would produce a weakness of the interaction strength between the olefins formed during the reaction and the metal surface. In this sense, results reported by Lieske et al. [23] evidenced that tin addition to Pt decreases the adsorption bond strength of 1-hexene. Hence, the olefins produced during the reaction are quickly desorbed from the metallic surface. Thus, the metallic centers would stay free of coke precursor hydrocarbons.

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