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Effect of tin addition on propane dehydrogenation reaction over silica-supported palladium-tin catalysts

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Abstract

The effect of Sn addition on the catalytic properties of Pd-Sn/SiO_2 catalysts for propane dehydrogenation was studied. Catalysts were prepared by the incipient wetness impregnation technique using $Pd(NO_3)_2$ or $PdCl_2$ and $SnCl_4$ precursors, varying the atomic Sn/Pd ratio between 0 and 1.0. The impregnating solutions were investigated by UV-vis spectroscopy, and the prepared catalysts were characterized by X-ray fluorescence (XRF), temperature-programmed reduction (TPR) and CO chemisorption. The UV-vis results revealed the existence of $Pd(H_2O)_4^{2+}$ and $PdCl_n(H_2O)_{4-n}^{2-n}$ complexes in the monometallic Pd solutions, and no Pd-Sn interaction in the bimetallic solutions. The reducibility of Pd in the fresh (uncalcined) and calcined catalysts depended on the nature of Pd precursor and the Sn/Pd ratio. The chemisorption results showed the CO/Pd ratio was not modified by the presence of tin, except for the catalyst with the lowest Sn/Pd ratio (Sn/Pd=0.1), which exhibited the highest CO/Pd ratio. This catalyst also gave the highest catalytic activity, while the rest of the catalysts presented similar lower activities. Propylene was the only product observed during the reaction, except during the first seconds of time on-stream, in which hydrogenolysis products (methane and ethane) were detected.

Keywords: Pd-Sn catalysts, propane dehydrogenation, tin addition, CO chemisorption.

Efecto de la adición de estaño en la deshidrogenación de propano en catalizadores de paladio-estaño soportado sobre sílice

Resumen

Se estudió el efecto del Sn sobre las propiedades catalíticas de catalizadores de Pd-Sn/SiO_2 para la deshidrogenación de propano. Los catalizadores se prepararon por impregnación a humedad incipiente, utilizando las sales $Pd(NO_3)_2$ o $PdCl_2$ y $SnCl_4$, para obtener relaciones atómicas Sn/Pd entre 0.1 y 1.0. Las soluciones de impregnación se estudiaron por espectroscopia UV-visible, y los catalizadores fueron caracterizados por fluorescencia de rayos X (XRF), reducción a temperatura programada (TPR) y quimisorción de CO. Los resultados de la espectroscopia UV-visible demostraron la existencia de los complejos $Pd(H_2O)_4^{2+}$ y $PdCl_n(H_2O)_{4-n}^{2-n}$ en las soluciones monometálicas de Pd, y en las soluciones bimetálicas de Pd y Sn no se observó ninguna interacción entre estos metales. La reducibilidad del Pd en todos los catalizadores depende de la sal de Pd

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utilizada y de la relación Sn/Pd. La relación CO/Pd no resultó afectada por la presencia de Sn, excepto para el catalizador con la menor relación Sn/Pd (Sn/Pd=0.1), obteniéndose la mayor relación CO/Pd. Este catalizador también exhibió la mayor actividad catalítica, mientras que el resto de los catalizadores presentaron actividades menores similares. El propileno fue el único producto observado durante la reacción, excepto durante los primeros segundos de los experimentos de actividad, en los que se observaron productos de hidrogenólisis (metano y etano).

Palabras clave: catalizadores de Pd-Sn, deshidrogenación de propano, adición de Sn, quimisorción de CO.

Introduction

The current chemical scenario shows an increased interest in light olefins, since they are the starting material for some of the most important chemical products, such as polymers, synthetic rubbers and oxygenated compounds for reformulated fuels, which include methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE), and tertiary amyl methyl ether (TAME). The dehydrogenation of light paraffins provides an interesting way to exploit natural gas liquids (NGL) sources by converting these hydrocarbons into olefins, which in turn can be transformed into more valuable chemicals (1).

In the last years, paraffins dehydrogenation has been investigated on platinum-based catalysts, particularly on bimetallic Pt-Sn catalysts (2-5), because the monometallic Pt catalysts quickly deactivate by the formation of coke. Few studies are related to this reaction on supported Pd catalysts (6-11). Palladium, which belongs to the same platinum group and is less expensive, could be a suitable metal for dehydrogenation. Vallecillos *et al.* (6) studied the dehydrogenation of propane over Pd/Al_2O_3 and Pd-Sn/Al_2O_3 catalysts prepared with different source and dose of Sn, and found that the Sn addition diminished the initial activity of palladium, but increased the dehydrogenation selectivity and improved the catalytic stability. Masai *et al.* (8) studied the hydrogenation and dehydrogenation activity of Pd-Sn/SiO_2 catalysts, and Rodriguez (9) studied the n-butane dehydroisomerization on Pd-Sn/Al_2O_3 catalysts. They found best performances for certain Sn/Pd ratios.

On the other hand, Rodriguez *et al.* (11) studied the dehydrogenation of butane over Pd-Ga/Al_2O_3 catalysts with different atomic Ga/Pd ratios, and they found that the effects of Ga were the same as those caused by the Sn in the mentioned Pd-Sn/Al_2O_3 catalysts for the dehydrogenation.

The aim of this work is to study the effect of Sn addition on the catalytic properties of supported Pd-Sn catalysts for propane dehydrogenation. Silica was chosen as support due to its acidity deficiency, so it can not promote the cracking reactions that affect selectivity towards olefins.

Materials and methods

Catalysts preparation

The monometallic Pd and Sn catalysts were prepared by incipient wetness impregnation of silica with aqueous solutions of $Pd(NO_3)_2$ (Fisher, >99%) in 0.16 M HNO_3 and $SnCl_4$ (Aldrich, >99%) in 0.10 M HCl, respectively. The bimetallic Pd-Sn catalysts were prepared by co-impregnation using mixtures of these solutions in appropriate proportions. In addition, another monometallic Pd catalyst was prepared using an aqueous solution of $PdCl_2$ (Fisher >99%) in 0.10 M HCl. Silica (Baker) was crushed and sieved, taking the fraction with particle sizes of 60/80 mesh, which was calcined at 700 °C for 4 h. The nominal contents of metals in the catalysts were 0.5 wt.% Pd and 0-0.56 wt.% Sn, so that the Sn/Pd atomic ratio varied between 0 and 1. The catalysts were studied in the fresh (as prepared) and calcined states. Catalyst calcination was carried out at 500 °C for 2 h. Catalyst composition were measured in a Shimadzu 700HS energy dispersive X-ray fluorescence spectrometer, provided with an Rh gun operated at 50 keV. Table 1 summarizes the identification and the composition of catalysts.

Characterization

The UV-vis spectra of the impregnating solutions were measured in a Perkin-Elmer Lambda 2 spectrometer. The spectra were recorded in the 190-700 nm range. The TPR profiles were measured from -50 to 700 °C in a Vycor U-tube reactor connected to a conventional gases system equipped with a thermal conductivity detector (TCD), using a mixture of 5% H_2/Ar as reducing gas. Prior to measurement, the catalyst sample (100 mg) was dried at 110 °C in a flow of Ar for 1 h (fresh catalyst) or calcined as explained before, then cooled down in flowing Ar from 150 °C to room temperature and, then, to -50 °C, using an isopropanol-liquid nitrogen bath, before admitting the flow of the reducing gas. The reactor was freely heated from –50 to 15 °C after removing the cool bath, and immediately heated to 700 °C at 0.167 °C s^{-1}, using a temperature-controlled furnace. CO chemisorptions were carried out on the calcined catalysts (200 mg), sending CO pulses (46 μL) at room temperature, using He (0.5 mL s^{-1}) as a carrier gas. For these experiments, the catalysts were previously reduced at 500 °C in flowing H_2 for 1 h, and the adsorbed hydrogen was removed by flushing He at 500 °C for 1 hour.

Catalytic activity

The propane dehydrogenation reaction was carried out at 500 °C and atmospheric pressure, under differential conditions (i.e. propane conversion less than 10%) in a conventional reaction line, built in stainless steel. A Vycor U-tube (6 mm OD) reactor was charged with 50 or 80 mg of catalyst (calcined), which was previously reduced at 500 °C. The reaction mixture contained hydrogen and propane with a H_2/C_3H_8 ratio of 16/1 and a total flow of 1.42 mL s^{-1}. Reaction products were analyzed in a Perkin-Elmer GC, equipped with an Alumina F1 packed column and a flame ionization detector (FID).

Results and discussion

UV-vis study of impregnating solutions

The UV-vis spectra of Pd and Sn solutions are shown in figure 1. For the $Pd(NO_3)_2$ solution, two absorption bands are observed at 286 and 376 nm, due to the electronic transitions in the free NO_3^- ions and *d-d* transitions in the tetra-aqua complex

Table 1

Identification, composition and CO/Pd ratio of Pd and Pd-Sn catalysts

Fresh catalysts	Calcined catalysts	Pd (wt.%)	Sn (wt.%)	Cl[b] (wt.%)	Sn/Pd	CO/Pd
Pd-*F*	Pd-*C*	0.47	0	0	0	0.026
SnPd-0.1*F*	SnPd-0.1*C*	0.38	0.06	N.D.	0.14	0.043
SnPd-0.5*F*	SnPd-0.5*C*	0.42	0.18	0.13	0.38	0.021
SnPd-1*F*	SnPd-1*C*	0.45	0.42	0.17	0.84	0.024
Pd-*F*Cl[a]	Pd-*C*Cl[a]	0.35	0	0.13	0	-

N.D.: not detected. [a]: samples prepared from $PdCl_2$. [b]: measurements carried out in fresh catalysts. In the calcined catalysts the presence of chlorine was not detected by XRF.

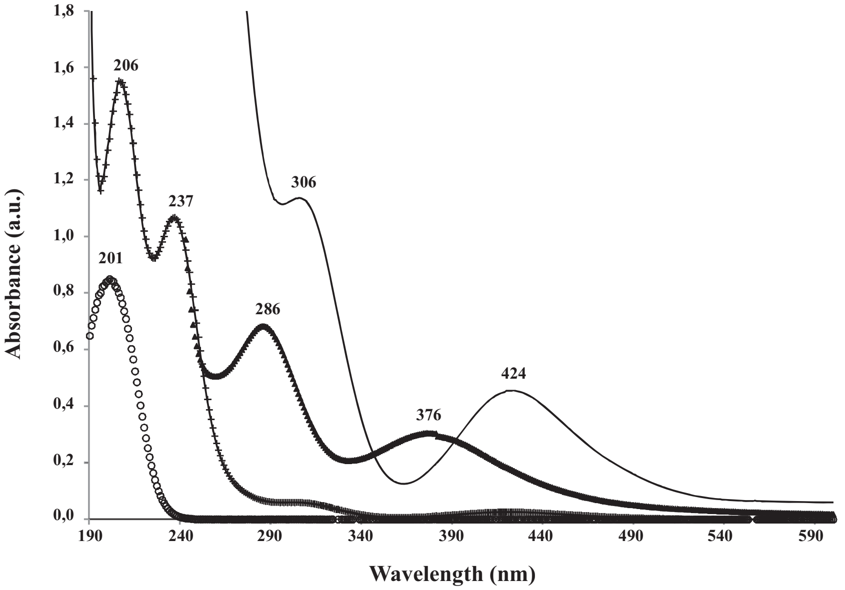

Figure 1. UV-vis spectra of the Pd and Sn impregnating solutions: (—) $PdCl_2$ in HCl; (+) $PdCl_2$ in HCl diluted with deionized water in a ratio of 1/5 (-▲-) $Pd(NO_3)_2$ in HNO_3; (-○-) $SnCl_4$ in HCl.

$Pd(H_2O)_4^{2+}$, respectively (12). These results show the non-complexing behavior of nitrate ions towards palladium atom centers.

On the other hand, the spectrum of $PdCl_2$ solution presents four absorption bands centered at 206, 237, 306 and 424 nm. The first two bands are very intense in the UV region and could be well-resolved in the spectrum after diluting the solution with deionized water in a water/solution ratio of 1/5. The four bands have been assigned to electronic transitions of square-planar $PdCl_n(H_2O)_{4-n}^{2-n}$ complex, with $1 \leq n \leq 3$ (13). The bands at 206 and 237 nm have been described as ligand-to-metal charge transfer transitions and the bands at 306 and 424 nm as *d-d* transitions (13). These results show that Cl^- ions coordinate with palladium centers, contrasting with the behavior of NO_3^- ions. For the $SnCl_4$ solution, only an absorption peak at 201 nm was found, and it has been attributed to Sn^{2+} and/or Sn^{4+} species (14, 15).

The UV-vis spectra of the bimetallic Pd-Sn solutions as a function of Sn/Pd ratio are shown in figure 2. These solutions were prepared with monometallic solutions of $Pd(NO_3)_2$ and $SnCl_4$ in diluted HCl. For the solution with a Sn/Pd = 0.1 (spectrum 2a), two distinguishable absorption bands are centered at 282 and 381 nm, which have been attributed to *d-d* transitions (13). These bands shifted to 289 and 399 nm, respectively, for the solution with a Sn/Pd = 0.5 (spectrum 2b), and to 300 (as a shoulder) and 405 nm for the solution with Sn/Pd = 1 (spectrum 2c). The increase in Sn/Pd ratio of the bimetallic solutions implied a parallel increase in the Cl^- concentration, since Cl^- ions came from the aqueous hydrochloric $SnCl_4$ solution. This caused changes in the UV-vis spectra of the bimetallic solutions from the spectral features corresponding to the $Pd(NO_3)_2$ solution to those characteristics of the $PdCl_2$ solution (figure 1). Some H_2O ligands of the $Pd(H_2O)_4^{2+}$ species present in the $Pd(NO_3)_2$ solution were replaced by Cl^- ions coming from $SnCl_4$ solution. However, the UV-vis results indicate no Pd-Sn interactions in these bimetallic solutions (16).

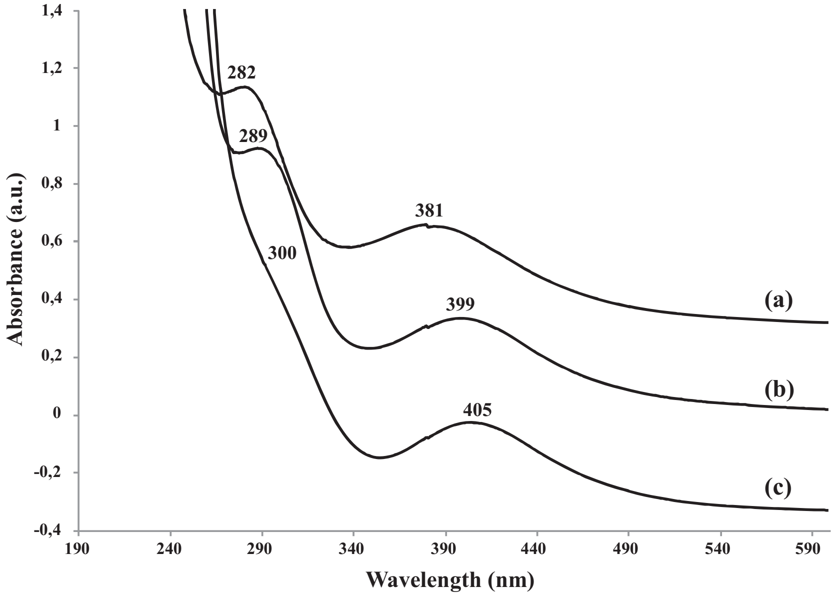

Figure 2. UV-vis spectra of bimetallic Pd-Sn solutions as a function of Sn/Pd ratio. a) Sn/Pd = 0.1; (b) Sn/Pd = 0.5; (c) Sn/Pd = 1.

Reduction properties of supported Pd and Sn species

The TPR profiles of the fresh catalysts are shown in figure 3A. The Cl-free Pd catalyst (Pd-*F*) gave a peak centered at 92 °C and a shoulder at around 145 °C. They can be attributed to the reduction of $Pd(NO_3)_2$ particles (17). The higher temperature of the shoulder could be caused by a moderate interaction between the smaller $Pd(NO_3)_2$ particles and the support surface.

The TPR profiles of the bimetallic catalysts presented progressive changes with the addition of increasing quantities of Sn. In fact, the concomitant rising amount of HCl solution used in their preparations could cause these changes. Thus, the SnPd-0.1*F* catalyst showed a small peak at 54 °C and an intense peak at 128 °C, preceded by shoulder at 92 °C and followed by a slight shoulder at 145 °C. Due to the low reduction temperature, the peak at 54 °C can be assigned to the reduction of PdO particles (18-20). The shoulders at 92 and 145 °C can correspond to the reduction of $Pd(NO_3)_2$ particles, according with the assignments proposed for the monometallic Pd-*F* catalyst. The peak at 128 °C can be attributed to the reduction of Pd species that were partially coordinated with Cl^- ions, in concordance with UV-vis results. The SnPd-0.5*F* and SnPd-1*F* catalysts exhibited an intense peak at 164 y 156 °C, respectively, which is sharper than the peak at 128 °C, and similar to that corresponding to the Pd-*F*Cl catalyst, which showed a sharp peak at 153 °C. In addition, these bimetallic catalysts presented a color (orange) analogous to that observed in the Pd-*F*Cl catalyst, which was prepared with $PdCl_2$. Therefore, the peak observed for the bimetallic catalysts can be assigned to reduction of this salt.

On the other hand, the wide peak observed at 350 °C for the SnPd-1*F* (figure 3A, insert) can be attributed to the reduction of Sn^{4+} to Sn^{2+} and/or Sn^0 species assisted by Pd^0 via spillover (2, 21, 22). In general, the tendency in the changes observed in the TPR profiles for the fresh catalysts are in parallel with the trend in the UV-vis results for the solutions used in the preparation of these

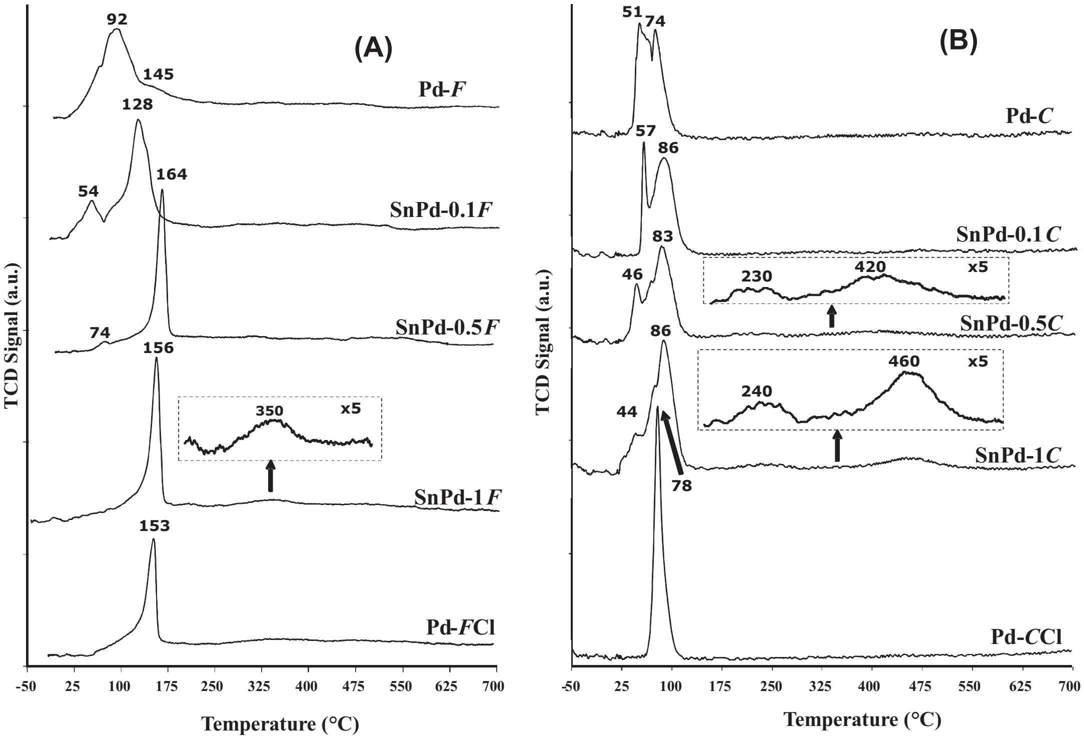

Figure 3. TPR profiles of the fresh (A) and calcined (B) silica-supported Pd and Pd-Sn catalysts.

catalysts, where the absorption bands changed as the Sn/Pd ratio was increased.

The TPR profiles of the calcined catalysts are shown in figure 3B. The Pd-*C* catalyst showed two overlapped peaks with maxima at 51 and 74 °C, which have been assigned to the reduction of PdO particles with bimodal distribution of particle size (18-20). In contrast, the Pd-*C*Cl catalysts showed an intense single peak at 78 °C, suggesting that there were only small PdO particles on the support surface. Evidently, the nature of Pd precursor affected the size of PdO particles formed during the calcination treatment, where the Cl-containing Pd salt favored the formation of the smaller ones.

The calcined bimetallic catalysts also presented changes as the Sn/Pd ratio was increased. But, in this case, these changes cannot be attributed to the presence of HCl since it was removed from the catalyst after calcinations (table 1). For the SnPd-0.1*C* catalyst, the PdO reduction peaks are observed at higher temperatures (57 and 86 °C) and with different shapes in comparison with those shown by the Pd-*C* catalyst. The low-temperature peak resulted sharper and the high-temperature peak broader. This indicates that the addition of a very small amount of Sn could cause an increase in the proportion of small-to-large PdO particles during the calcination of the catalyst. Increments in the Sn content led to shift the low-temperature peak to lower temperatures (46 and 44 °C) and decrease its intensity, while the high-temperature peak kept at the same temperature (86 °C) and became more intense. This constancy in the reduction temperature of the second peak, contrasting with the expected tendency to shift to the reduction temperature (78 °C) exhibited by the Pd-*C*Cl catalyst due to the effect of the added HCl observed for the fresh bimetallic catalysts in Figure 3B, suggests that a small fraction of tin species is simultaneously reduced with the smaller particles of PdO. Additionally, the peaks observed around 230-460 °C (figure 3B, inserts) have been attributed to the reduction of Sn^{4+} species to Sn^{2+} and/or Sn^0 via spillover (2, 23). In consequence, the formation of Pd-Sn solid solutions could take place during the reduction of the bimetallic catalysts, particularly in those with the higher Sn/Pd ratios (23).

CO Chemisorption

The values of CO/Pd ratio for the calcined catalysts are presented in Table 1. These values resulted very small for all the catalysts, indicating that they exhibited very low Pd dispersions. The CO/Pd ratio was little affected by the presence of tin in the bimetallic catalysts, except for the catalyst with the lower Sn/Pd ratio (SnPd-0.1*C*), which showed a higher value than that corresponding to the monometallic catalyst. This is in parallel with the increase in the amount of smaller PdO particles with respect to larger PdO particles, indicated by the comparison of the TPR profiles of this catalyst and of the Pd-*C* catalyst (figure 3B).

The further decrease in CO/Pd ratio with the increasing Sn content is consistent with the blocking effect of Sn on the surface of Pd particles. But, the true decrease in the Pd dispersion could be bigger than this decrease in CO/Pd ratio. Changes in the stoichiometry of CO adsorption on Pd due to the addition of Sn, considering the different forms of adsorbed CO, has been reported by Sales *et al.* (23). They attributed this result to a dilution effect of Pd atoms by Sn atoms, diminishing the probability of formation of bridged CO species. On the other hand, Sn can also induce an electronic effect on Pd and, in consequence, on the CO adsorption on bimetallic Pd-Sn catalysts (8).

Dehydrogenation of propane

The variation of catalytic activity with the time on-stream (TOS) for the propane dehydrogenation over calcined catalysts is shown in figure 4. In general, the activity decreased slightly with TOS, except the SnPd-0.1C catalyst, which showed a strong diminution from 4800 s on stream. This deactivation is due to the formation of carbo-

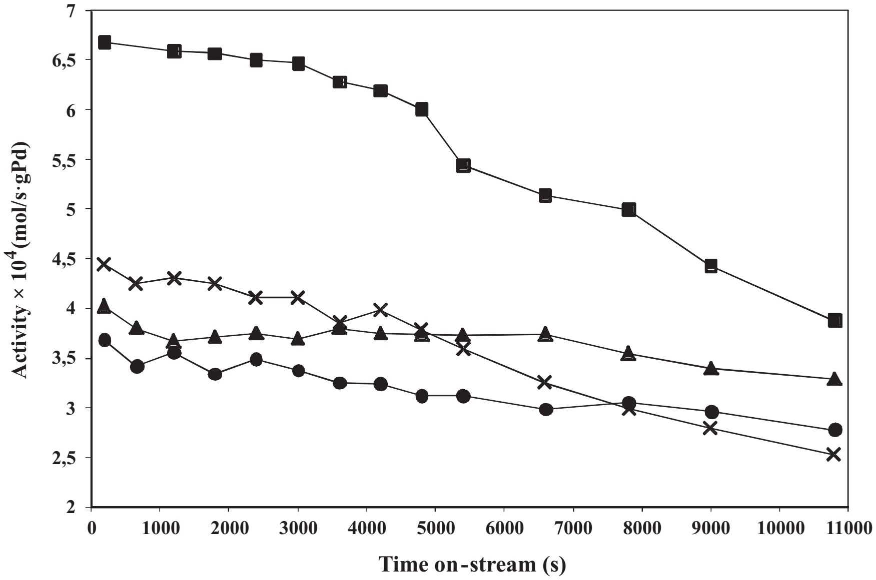

Figure 4. Variation of catalytic activity with the time on-stream for propane dehydrogenation over Pd/SiO_2 and Pd-Sn/SiO_2 catalysts: (▲) Pd-*C*; (■) SnPd-0.1*C*; (●) SnPd-0.5*C*; (×) SnPd-1*C*.

naceous residues (coke) on the surface of Pd particles.

The low deactivation during the first 4800 s on stream and initial propylene selectivities of 100% observed in this work contrast with the strong deactivation in the first 1800 s on stream and low initial propylene selectivities reported for Pd-Sn/Al_2O_3 catalysts, proved in the propane dehydrogenation at the same conditions (6). This could be due to one of the following reasons: (i) a fast formation of coke rapidly deactivated the catalyst (before analyzing the first reactor effluent sample at the third minute on stream), or (ii) a slow formation of coke due to a low catalytic activity. In order to elucidate the effect of the coke deposition on the activity of the catalysts during the first seconds on stream, experiments were carried out measuring the activity at 30 s on stream for the Pd-*C* and SnPd-0.1*C* catalysts.

The catalytic activities at 30 s on stream were significantly higher (7×10^{-4} and 13×10^{-4} mol/(sgPd), respectively) than those at 180 s of TOS, shown in the figure 4. Again, the SnPd-0.1*C* catalyst was the most active.

In addition, at 30 s on stream, methane and ethane (hydrogenolysis products), along with propylene were detected, resulting dehydrogenation selectivities about 54% for both catalysts. These results indicate that the catalysts were rapidly deactivated before the third minute on stream by coke deposition on the most active Pd sites. On the other hand, a small dose of tin (Sn/Pd = 0.1) promoted the activity of Pd sites, decreasing the strength of propane adsorption and, in consequence, decreasing the rate of coke formation, whereas for higher amounts of Sn added to the Pd catalyst (Sn/Pd > 0.1), the surface Pd atoms were blocked by Sn atoms in higher extent, which explains the results observed in figure 4.

The higher activity exhibited SnPd-0.1*C* is in agreement with its higher dispersion. Valecillos *et al.* (6) found similar results in Pd-Sn/Al_2O_3 catalysts. They rationalized the results in terms of the site-blocking effect of Sn and its repulsive interactions with the adsorbed hydrocarbon species. The higher activity for the Sn/Pd ratio of 0.1 is also in good agreement with the results reported by Masai *et al.* (8) in the cyclohexane dehydrogenation over Pd-Sn/SiO_2 catalysts. These authors attributed their results to electronic effects of Sn on Pd, where the presence of Sn weakens the hydrocarbon adsorption on Pd in the tin-containing catalysts. When the strength of hydrocarbon adsorption on Pd is high, the adsorbed hydrocarbon species can suffer the rupture of C-H (dehydrogenation) and C-C (hydrogenolysis) bonds. But, when the hydrocarbon adsorption is weakened, the fission of C-C bonds is hindered, favoring the dehydrogenation reactions.

Measurements of n-butane dehydroisomerization carried out on Pt-Sn/Al_2O_3 (9) showed that activity and selectivity increased with the Sn/Pt ratio between 0.21 and 0.71, and the authors concluded that Sn hinders the deposition of coke on Pt sites. In turn, the Sn effect was favored by the presence of chloride in the Pt-Sn/Al_2O_3 catalysts. Moreover, Sn may help the transport of coke to the support, leading to the increased in the dehydrogenation selectivity. Those results contrast with that observed in this research. In summary, the TPR profiles suggested that the extent of Pd-Sn interaction increased with Sn content. However, this behavior is not reflected in the activity results, since the activity did not change continuously with the Sn/Pd ratio. On the other hand, the activity seems to correlate with the results obtained by CO chemisorptions, that is, the catalyst with higher CO/Pd ratio showed the higher activity for propane dehydrogenation.

Conclusions

No evidence of Pd-Sn interactions in the bimetallic $Pd(NO_3)_2$ and $SnCl_4$ solutions was found. TPR results of the fresh catalysts suggest the existence of PdO and $Pd(NO_3)_2$ for Sn/Pd ≤ 0.10, and PdO and $PdCl_2$ species for Sn/Pd > 0.10 for the fresh catalysts. For the calcined monometallic catalysts, there were two different sizes of PdO particles when a Cl-free Pd precursor was used in the catalyst preparation, and only one size of PdO particles was observed when Cl-containing Pd precursor was used. The CO/Pd ratio was little affected by Sn addition, except in the case where the smaller amount of Sn was used (Sn/Pd=0.1), giving the higher CO/Pd ratio. The formation of coke strongly decreased the catalytic activity, and increased the dehydrogenation selectivity. The catalytic activity correlated with de CO/Pd ratio. After 180 s on stream, the catalytic stability was high and the dehydrogenation selectivity was 100%, but hydrogenolysis products were detected at lower TOS.

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