CIENCIA 14 (Special Number on Adsorption and Catalysis), 125 - 134, 2006
Maracaibo, República Bolivariana de Venezuela

Propane dehydrogenation over alumina-supported palladium and palladium-tin catalysts

*José Valecillos, Douglas Rodríguez, Jonathan Méndez, Roger Solano, Carlos González, Thaís Acosta, Jorge Sánchez and Geomar Arteaga**

Instituto de Superficies y Catálisis, Facultad de Ingeniería, Universidad del Zulia, Maracaibo 4003A, Apartado 15251, Venezuela

Received: 23-01-06 Accepted: 04-03-06

Abstract

The dehydrogenation of propane over Pd/Al_2O_3 and $Pd\text{-}Sn/Al_2O_3$ catalysts was studied as a function of Sn content, addition of chlorine, and reaction time. Bimetallic catalysts were prepared by incipient wetness impregnation of a Cl-free $Pd/\gamma\text{-}Al_2O_3$ catalyst with solutions of $SnC_4H_4O_6$ (tin tartrate) and $SnCl_2$ + HCl. Atomic Sn/Pd ratios were 0.07 and 0.22 for the Cl-containing catalysts, and 0.04 for the Cl-free catalyst. The catalysts were calcined at 400°C and reduced in H_2 at 500°C. These materials were characterized by temperature programmed reduction (TPR) and H_2 and CO chemisorption. The reaction was carried out at 500°C and a molar H_2/C_3H_8 ratio of 16. The addition of Sn strongly modified the CO adsorption on Pd, particularly when Cl was present. In contrast, H_2 adsorption was not affected by Sn addition. TPR profile of Pd/Al_2O_3 showed two peaks at 5 and 18°C, attributed to the reduction of large and small PdO particles, respectively. The formation of β-palladium hydride phases was evidenced by two negative peaks of H_2 desorption at 61 and 85°C. The addition of Sn caused (i) the diminution in size of the large PdO particles, resulting a symmetrical peak at 15°C, (ii) a small peak at 53°C, ascribed to the reduction of a small fraction of SnO_2 assisted by Pd°, and (iii) the formation of a β-PdH phase, which produced a negative peak at 72°C. Initial activity of Pd/Al_2O_3 was high, but it deactivated due to coking. Coke had a strong negative effect on hydrogenolysis reactions, increasing the dehydrogenation selectivity. With the addition of Sn, the initial activity of Pd decreased, the dehydrogenation selectivity increased and the catalytic stability improved. Tin and coke had similar effects on catalytic properties of Pd/Al_2O_3. The results were rationalized in terms of the site-blocking effect of Sn and of its repulsive interactions.

Key words: CO chemisorption; H_2 chemisorption; Pd/Al_2O_3; $Pd\text{-}Sn/Al_2O_3$;; propane dehydrogenation; TPR.

Deshidrogenación de propano sobre catalizadores de paladio y paladio-estaño soportados sobre alúmina

Resumen

Se estudió la deshidrogenación de propano sobre catalizadores de Pd/Al_2O_3 y $Pd\text{-}Sn/Al_2O_3$ en función del contenido de Sn, la adición de cloro y la coquización. Los catalizadores bimetáli-

---

* Autor para la correspondencia. Telef. 58-261-7598797, E-mail: garteaga@luz.edu.ve

cos fueron preparados por impregnación a humedad incipiente de un catalizador de Pd/γ-Al_2O_3 libre de cloro con soluciones de $SnC_4H_4O_6$ (tartrato de estaño) y de $SnCl_2$ + HCl. Las relaciones atómicas Sn/Pd fueron 0.07 y 0.22 para los catalizadores que contienen Cl y 0.04 para el catalizador libre de Cl. Los catalizadores fueron calcinados a 400°C y reducidos a 500°C. Estos materiales fueron caracterizados mediante las técnicas de reducción a temperatura programada (RTP) y quimisorción de H_2 y CO. La reacción se llevó a cabo a 500°C y a una relación molar H_2/C_3H_8 de 16. La adición de Sn modificó fuertemente la adsorción de CO sobre el Pd, particularmente cuando el cloro estaba presente. En contraste, la adsorción de H_2 no fue afectada por la adición de Sn. El catalizador de Pd/Al_2O_3 mostró dos picos de reducción a 5 y 18°C, atribuidos a la reducción de partículas de PdO grandes y pequeñas, respectivamente. La formación de fases de β-PdH se evidenció mediante dos picos negativos de desorción de H_2 a 61 y 85°C. La adición de Sn causó (i) la disminución en tamaño de las partículas de PdO grandes, resultando un pico simétrico a 15°C, (ii) un pico pequeño a 53°C, atribuido a la reducción de una pequeña fracción de SnO_2 asistida por Pd°, y (iii) la formación de una fase de β-PdH, el cual produjo un pico negativo a 72°C. La actividad inicial del catalizador de Pd/Al_2O_3 fue alta, pero se desactivó fuertemente debido a la coquización. El coque tuvo un fuerte efecto negativo sobre las reacciones de hidrogenólisis, incrementándose la selectividad de deshidrogenación. Con la adición de Sn, la actividad inicial del Pd disminuyó, la selectividad de deshidrogenación aumentó y la estabilidad catalítica mejoró. El estaño y el coque tuvieron efectos similares sobre las propiedades catalíticas del Pd/Al_2O_3. Los resultados fueron explicados en términos del efecto de bloqueo de sitio del estaño y de sus interacciones repulsivas.

Palabras clave: Deshidrogenación de propano; Pd/Al_2O_3; Pd-Sn/Al_2O_3; TPR; quimisorción de CO; quimisorción de hidrógeno.

Introduction

Olefins are raw materials for many useful products, particularly polymers such as polyethylene, polypropylene, polyvinyl chloride, and polybutadiene. The most important reactions to produce olefins at industrial scale are cracking and dehydrogenation of paraffins, which can be carried out through thermal or catalytic processes. Paraffin dehydrogenation is an endothermic reaction requiring very high temperatures to reach high conversions. In the thermal cracking, these conditions (800°C for light paraffins) favor many reactions: dehydrogenation, cracking, isomerization, coking, and acetylene formation. Coking causes coke deposition on the tube surface of reaction furnaces, originating heat transfer problems, whereas the other reactions lead to the formation of many by-products, which make the purification section more complex, increasing the investment and operational costs.

Catalytic dehydrogenation is an adequate alternative to avoid the troubles of thermal dehydrogenation. The use of a catalyst permits lower temperatures for the dehydrogenation of light paraffins, reaching satisfactory conversions and high selectivities. Alumina-supported chrome oxides (1) and alumina-supported platinum-tin (2) are catalysts used in this process. The dehydrogenation selectivity of supported Pt-Sn catalysts can be improved by adding sodium or potassium (3).

A catalytic system based on palladium, which is less expensive than platinum, seems to be an excellent option for paraffin dehydrogenation. Some studies involving the dehydrogenation of C_6 hydrocarbons over supported Pd catalysts (4-7) show that palladium may have a good role on the light hydrocarbon dehydrogenation. However, to the best of our knowledge, the performance of supported Pd catalysts for the dehydrogenation of light paraffins has not been reported.

Maatman *et al.* (4) studied the role of Pd/alumina in the dehydrogenation of cyclohexane to benzene at 175-210°C. Ramos *et al.* (5) studied the reaction pathways for C_6 hydrocarbons over model Pt catalysts. The main reactions were dehydrogenation and hydrogenolysis. The former was favored at high temperatures and low hydrogen/hydrocarbon ratios. Masai *et al.* (6) studied the dehydrogenation and hydrogenation activity of Pd-Sn/SiO_2 catalysts. They found that a small amount of tin promotes the activity for cyclohexane dehydrogenation over Pd, while large quantities of tin are unfavorable for dehydrogenation activity. Haro *et al.* (7) reported that Pt/Al_2O_3 catalysts are more active than Pd/Al_2O_3 for the cyclohexane dehydrogenation at 160-200°C. However, palladium could present a better catalytic behavior at the higher temperatures required for the dehydrogenation of light paraffins.

In this work, the catalytic performance of Pd/Al_2O_3 and Pd-Sn/Al_2O_3 catalysts for the dehydrogenation of propane at 500°C was study. The effects of Sn addition on catalytic properties of Pd were determined in the presence or absence of chlorides. The catalysts were characterized by H_2 and CO chemisorption and temperature programmed reduction (TPR).

Experimental

Catalyst preparation

A commercial Pd/γ-Al_2O_3 catalyst with low metal content was used in this study. The catalyst were crushed and sieved to obtain particle sizes in the range 0.18-0.25 mm (60/80 mesh). Three bimetallic Pd-Sn/Al_2O_3 catalysts with different Sn loading were prepared by incipient wetness impregnation of the monometallic catalyst with solutions of Cl-containing and Cl-free Sn precursors. Two catalysts with increasing Sn content were prepared using $SnCl_2.2H_2O$ (Aldrich) dissolved in a 0.1 M HCl solution, and one catalyst was prepared using tin tartrate, $SnC_4H_4O_6$ (Strem). This salt is slightly soluble in water and, therefore, the portion of non-dissolved salt was homogeneously dispersed in the solution by using an ultrasonic bath. The resulting cloudy solution was added to the catalyst as quickly as possible. The Pd-Sn/Al_2O_3 catalysts were dried at 110°C for 12 h. The Pd, Sn and Cl contents were measured by energy dispersive X-ray fluorescence spectroscopy (EDX) (Shimadzu EDX-700HS) and are listed in Table 1, along with the atomic Sn/Pd ratios and the Sn precursors of the bimetallic Pd-Sn/Al_2O_3 catalysts.

Chemisorption measurements

The measurements of H_2 and CO chemisorption were carried out using a stainless steel apparatus designed to work by pulses and to perform heat treatments *in*

Table 1
Composition and Sn precursor of the alumina-supported catalysts.

Catalyst	Pd content (wt.%)	Sn content (wt.%)	Cl content (wt.%)	Sn/Pd ratio	Sn Precursor
A	0.34	0	0	0	-
B	0.33	0.015	0	0.042	$SnC_4H_4O_6$
C	0.33	0.026	0.10	0.072	$SnCl_2$
D	0.34	0.085	0.52	0.221	$SnCl_2$

situ. The switching of gases was done without mixing or access of air. The H_2 and CO signals were measured using a thermal conductivity detector (TCD) (Gow Mac). The reactor was a U-shaped Vycor tube of 6 mm. A loop of 46 μL was used as calibrated volume for the gas pulses. Ar and He were used as carrier gases for the H_2 and CO chemisorption measurements, respectively. A catalyst sample of 250 mg was dried at 110°C for ½ h and calcined at 400°C for 1 h in a flow of air, then reduced at 500°C in a flow of H_2 for 1 h, purged at 300°C for ½ h and cooled to 22°C in a flow of Ar. After the TCD signal was stabilized, a succession of H_2 pulses was sent to the reactor until saturation. Then, using a flow of He, the sample was heated at 300°C for ½ h to remove the adsorbed hydrogen and cooled to 22°C, before CO chemisorption measurements. The flow of the gases was 30 mL/min. CO, Ar and He (99.999% of purity) were supplied by Praxair and H_2 was obtained from a Packard hydrogen generator provided with a molecular sieve trap.

TPR analysis

Temperature programmed reduction (TPR) experiments were also carried out using the adsorption apparatus with 5% H_2/Ar (Praxair) at a flow of 30 mL/min (reducing gas) and a catalyst sample of 250 mg. The outlet of the reactor was connected via a 4-way ball valve (Whitey) to the TCD system through a molecular sieve (Linde 4A) water trap. The catalyst sample was dried and calcined as explained before, cooled to room temperature in flowing air and then to -80°C using a cold bath (isopropanol + liquid N_2) in an Ar flow. At this temperature, the TCD was stabilized in the flow of reducing gas before heating. The sample was spontaneously heated from -80°C to room temperature by removing the cold trap and then heated to 500°C at 10°C/min using a PC provided with a data adquisition card (National Instruments). The TCD signal was monitored at 6-s intervals using a Fluke digital multimeter and the data were transferred to a PC.

Catalytic activity measurements

Catalytic activity measurements were carried out in a continuous–flow reaction system, using a fixed-bed reactor at 500°C, atmospheric pressure and a constant flow of a mixture of propane (Matheson 99.6%) and hydrogen (85 mL/min, H_2/C_3H_8 molar ratio of 16). Prior to reaction, the catalyst sample (20 mg) was subjected to an identical pretreatment to that used in the chemisorption experiments. The products and feeds were analyzed using an on-line HP 5890 Series II gas chromatograph with a flame ionization detector (FID) and a 27 m capillary column containing PoraPLOT Q as stationary phase.

Results and Discussion

H_2 and CO chemisorption

The H/Pd and CO/Pd values estimated from chemisorption results of all the catalysts are shown in Table 2. For the catalyst A, the H/Pd value was lower than the CO/Pd value. This difference can be due to the possible existence of compressed bridged CO species in direct interactions with linear CO species (8),

Table 2
H/Pd and CO/Pd values obtained from chemisorption data of the catalysts.

Catalyst	H/Pd	CO/Pd
A	0.19	0.29
B	0.22	0.18
C	0.21	0.06
D	0.20	0.05

which give CO/Pd adsorption stoichiometries higher than 1. Hydrogen adsorption is essentially in linear form with a H/Pd adsorption stoichiometry of 1 (9). Juszczyk *et al.* (10) also reported slightly higher CO/Pd values compared to H/Pd values for Pd/Al_2O_3 catalysts. However, other comparisons between the H/Pd and CO/Pd values have been reported in the literature. Marín-Astorga *et al.* (11) found similar H/Pd and CO/Pd values, but in some cases the H/Pd value was slightly higher than CO/Pd value. Burch and Urbano (12) observed that Pd dispersion measured by H_2 chemisorption was higher than that measured by CO chemisorption.

The CO/Pd values strongly decreased with Sn addition whereas the H/Pd values remained almost constant. The hydrogen adsorption capability of Pd was not affected by Sn in the range of Sn content used in this work, contrasting with the strong diminution in CO adsorption capability. The decrease in CO/Pd was already significant with the smaller dose of tin (0.015%Sn, Sn/Pd=0.042), which corresponds to the catalyst B. A Cl-free catalyst containing 0.054%Sn, Sn/Pd=0.142 (not shown in the table) gave a CO/Pd ratio equal to 0.15. A stronger decrease in CO/Pd was observed for the Cl-containing bimetallic catalysts (C and D), almost a sixth of that corresponding to the monometallic catalyst. The CO/Pd values were practically the same for the Cl-containing catalysts in spite of the different Sn contents. These results indicate that chlorine induced more pronounced effects of Sn on the CO chemisorption, even at the lower Sn content, causing an independence of the CO/Pd ratio with respect to the Sn content. This suggests that the presence of Cl favored the formation of surface Pd-Sn aggregates after reduction. The adsorption properties of these aggregates were not modified by increasing Sn content (or Sn/Pd ratio) from 0.026 to 0.085%. Therefore, the surface of these bimetallic aggregates could have the same Sn concentration and, hence, the same structure. Similar results were found for Pt-Sn/Al_2O_3 catalysts, where Cl favored alloying of tin and platinum (13) or promoted a greater intimacy between these metals (14), causing a strong decrease in the CO/Pt values compared to Pt catalysts.

According to the chemisorption results for the bimetallic catalysts, if the total number of surface Pd atoms is given by the H_2 chemisorption, assuming a H/Pd adsorption stoichiometry of 1 (9) and knowing that hydrogen does not adsorb on Sn atoms (15), then only a small fraction of the surface Pd atoms was capable of adsorbing CO molecules. This decreased CO chemisorption for Pd-Sn catalysts can be explained in terms of the isolation of Pd atoms by Sn atoms (8,15,16) and the repulsive interactions between CO and Sn (15). Sales *et al.* (8) and Verdier *et al.* (16) observed by FTIR of adsorbed CO on Pd-Sn catalysts that the linear adsorption form was predominant while bridge adsorption form was disappearing with increasing Sn/Pd ratio. They explained their results based on the dilution of Pd atoms by Sn atoms, which diminishes the number of bridge sites containing only Pd atoms. Tsub *et al.* (17) observed a decrease in CO chemisorption energy for Sn/Pd(100) surface alloys. Xu and Koel (15) ascribed the strong suppression of CO chemisorption on Sn/Ni(111) surface alloys to the repulsive Sn-CO interactions at the Ni-CO distance required for chemisorption, which are caused by the outward buckling of Sn atoms on the bimetallic surface. By analogy, we could expect similar effects of Sn atoms on CO chemisorption over Pd-Sn/Al_2O_3 catalysts. In contrast, the amount of chemisorbed hydrogen on atop sites (linear species) was not affected by repulsive interactions between H and Sn because of the larger H-Sn distance of chemisorbed hydrogen on Pd. This is due to the smaller size of hydrogen atom.

Temperature-programmed reduction (TPR)

Reduction peaks at temperatures ranging from -80 to -50°C and from 200 to

500°C were absent in TPR profiles of all the catalysts, so only the temperature range of interest is shown in Figure 1. The catalyst A shows an intense, asymmetric peak at 18°C and two negative peaks at 61 and 85°C. The asymmetric peak exhibits a large shoulder at 5°C and a tail toward the higher temperature side. This peak has been ascribed to the reduction of crystalline PdO to Pd° (8, 11, 18, 19). These PdO particles may be dispersed on the alumina surface. The shoulder can be also attributed to the reduction of crystalline PdO to Pd° but forming larger particles, which present weak interactions with the support surface. Sales *et al.* (8) observed two reduction peaks at sub-ambient temperatures for a Pd/Al_2O_3 catalyst and these peaks were attributed to the reduction of two palladium oxide species differently interacting with the support. The negative peak at 61°C is more intense than the peak at 85°C, and both peaks result from the decomposition of the β-PdH phases, which are formed by hydrogen absorption during low temperature reduction of PdO (8, 18-21).

The catalyst B shows a more intense peak at 18°C, a small peak at 53°C and two closer negative peaks at 65 and 81°C. The addition of tin caused: (i) an increase in the intensity of the peak at 18°C in parallel to a weakening of the shoulder at 5°C, suggesting a disruption of the larger PdO particles, (ii) the appearance of the peak at 53°C, which can be ascribed to the reduction of SnO_2 to Sn° assisted by Pd atoms (8), (iii) a shift in the two negative peaks toward intermediate temperatures, resulting one peak at 72°C for the higher Sn/Pd ratio (0.221), and (iv) an increase in intensity of the high-temperature negative peak. The low intensity of the peak at 53°C indicates that a small fraction of the tin present in the catalyst was reduced.

For the Cl-containing bimetallic catalysts, the low temperature shoulder disappeared completely and the intense peak shows a symmetrical shape, particularly for the D catalyst which contained the higher Sn content. When the Sn content increases from 0.026 to 0.085 %, the intense peak also shows a slight shift toward lower temperatures with the maximum changing from 18 to 15°C. These results indicate that the addition of Sn causes a homogenization of the PdO particles supported on alumina and that further increase in Sn content has a small additional effect. These catalysts also show a peak at 53°C (at 58°C for the catalyst C) and only the high temperature negative peak. As for the Cl-free Pd-Sn catalyst, the small peak at 53°C indicates the reduction of a small amount of the tin oxide present in the Cl-containing catalysts. This reduction temperature for SnO_2 is very low compared to that reported by Sales *et al.* (8), who assigned a peak at 150°C to the reduction of Sn ions and of Pd ions surrounded by Cl^- for calcined Pd-Sn catalysts prepared using

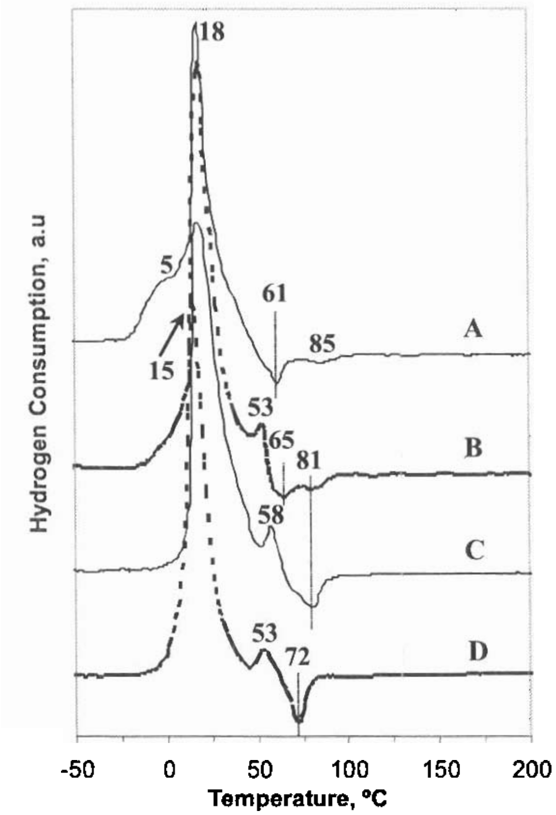

Figure 1. TPR profiles of the calcined catalysts.

$PdCl_2$ and $SnCl_2$. The high Cl content of these catalysts induced a higher reduction temperature for Sn as for Pd. The reduction temperatures are higher for chloride or oxychloride species than for oxide species (22).

As Sn content was increased for Cl-containing catalysts, the peak at 53°C became slightly broader, the low temperature negative peak disappeared, and the high temperature negative peak was slightly more intense and shifted from 81 to 72°C. This suggests the formation of Pd-Sn bimetallic particles after the reduction of SnO_2 assisted by Pd. On the other hand, no evidence of the reduction of palladium oxychlorides (PdO_xCl_y) was observed despite the presence of Cl in these catalysts. These species give a reduction peak at *ca.* 110°C (22).

Catalytic activity

The catalytic performance of the catalysts was determined for the propane dehydrogenation reaction at 500°C and atmospheric pressure. Figure 2 presents the evolution of the propane conversion as a function of the time on stream. The conversion decreased with time for all the catalysts. For the catalyst A, the decrease was large in the early stages of reaction but much less at longer times. The addition of tin sensibly decreased the deactivation rate of Pd as a result of a strong diminution in the initial activity, improving the catalytic stability of the bimetallic catalysts. The constancy in conversion after 30 min on stream for the Pd-Sn catalysts contrasts with the continuous decrease in conversion for the monometallic catalyst, which could be completely deactivated after a relatively shorter time on stream.

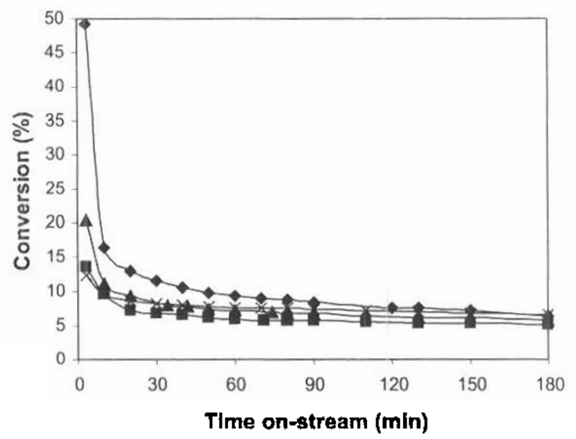

Figure 2. Propane conversion as a function of the time on-stream for all the catalysts: ♦ A, ■ B, ▲ C, × D.

This deactivation has been attributed to the deposition of coke on the catalyst surface by blocking reaction sites of the metal surface (6). Similarly, the strong decrease in initial activity caused by tin addition is due to its deposition on the active metal surface. In both cases, the most active Pd sites for propane reactions were the most affected. This is consistent with the strong decrease in CO chemisorption caused by the addition of tin. The presence of tin, in addition to its site blocking effect, can also weaken the adsorption of propane on Pd atoms as a consequence of repulsive interactions between the paraffin and Sn. Therefore, the adsorbed propane molecules on Pd atoms are less dehydrogenated and, thereby, the coke precursors are formed at lower rates, reducing the deactivation by coking. These effects of tin and coke on the activity are similar to those observed for $Pt\text{-}Sn/Al_2O_3$ catalysts (14).

The addition of Cl along with Sn to Pd/Al_2O_3 also had a promoting effect on the activity. This is evident on comparing the initial activities of the catalysts B and C (Figure 2), where the latter that contained Cl was more active than the former, which was a Cl-free catalyst with a lesser tin content. This result is opposed to the chemisorption results for these catalysts. The catalyst C presented the lower CO/Pd value and both catalysts gave the same H/Pd value (Table 2). Improvements of the activity by the presence of Cl were not observed for the higher Sn content despite the higher increase in Cl content (Table 1), indicating that the unfavorable effect of Sn on catalytic activity of Pd was stronger than the beneficial effect of Cl.

Table 3 shows the conversion and turnover frequency (TOF) values at 180 min on stream for all the catalysts. TOFs were estimated for this time due to the low conversions (%) and, under these conditions, the concept of differential reactor is applicable. On the other hand, TOFs are referred to the number of surface Pd atoms, which was estimated based on the H_2 chemisorption results. TOFs are similar for all the catalysts at the stationary conditions, confirming that both coke and tin have the same effect on the activity of Pd-Sn/Al_2O_3 catalysts for propane reactions.

All the selectivity data obtained in the present study cannot be presented here. Figure 3 constitutes only a small part of the total available data on which this discussion is based. The products of the reactions of propane over Pd/Al_2O_3 and Pd-Sn/Al_2O_3 catalysts were propylene (dehydrogenation) and methane (hydrogenolysis). "Initial" and "final" selectivities reported for dehydrogenation correspond to 3 and 180 min on stream, respectively. In Figure 3, the hydrogenolysis selectivity is obtained by subtracting the dehydrogenation selectivity from 100.

Initially, hydrogenolysis was the dominant reaction for the monometallic catalyst, but the rate of this reaction strongly dropped with increasing time on stream and dehydrogenation becomes the main reaction. It is well known that dehydrogenation is a structure-insensitive reaction and hydrogenolysis is a typical structure-sensitive reaction. Evidently, coking has strong effects on the structure-sensitive reaction, and favors dehydrogenation at the expense of hydrogenolysis. The high initial selectivity for hydrogenolysis of the Pd catalyst can be explained by a mechanism in which strong propane adsorption occurs on the most active sites constituted by adjacent Pd atoms. On these sites, the C–C bonds of the adsorbed paraffin molecules are readily broken and then the formed hydrocarbon fragments (CH_{4-n}) are rapidly hydrogenated to methane. At the same time, some adsorbed hydrocarbon molecules undergo a deep dehydrogenation producing coke precursors. The formation of coke on the metal surface modifies the catalyst selectivity by blocking a part of the surface Pd atoms of the large exposed Pd ensembles and, thereby, reducing the size of the most active sites (14), where hydrogenolysis reactions take place to produce methane.

The dehydrogenation of propane was also carried out over the catalyst A in the absence of H_2 in the reactor feed. Only propylene in small quantities was obtained despite the excessive coking. Coke formed on the catalyst surface was easily observed after reaction due to the change in color of the catalyst from light grey to intense black. The absence of H_2 favored the deep dehydrogenation of adsorbed hydrocarbon species and the condensation of these species formed large carbonaceous molecules (with low H/C ratio) on the catalyst surface. Finally,

Table 3
Conversion and TOF values at 180 min on stream for all the catalysts.

Catalyst	Conversion, %	TOF, s^{-1}
A	6.3	1.7
B	5.1	1.2
C	5.8	1.4
D	6.5	1.6

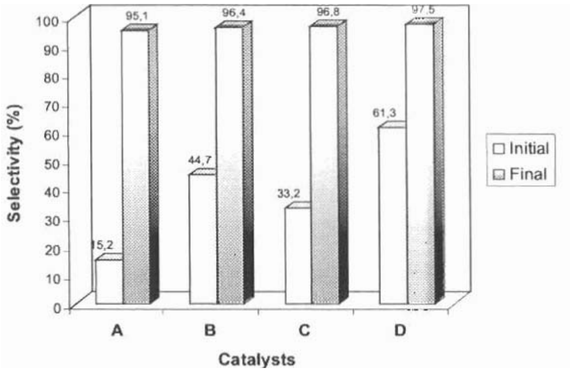

Figure 3. Initial and final selectivities to the dehydrogenation product for the catalysts.

the lack of methane formation shows that the catalyst selectivity is strong dependent of the absence or presence of H_2 in the gas phase.

In contrast to the behavior of the monometallic catalyst, the bimetallic catalysts show high dehydrogenation selectivities from the beginning of reaction. This indicates that tin addition inhibited the hydrogenolysis reactions on Pd sites, favoring dehydrogenation selectivity. As for coke, tin blocked some Pd atoms of the most active sites and reduced the size of these sites. A weakened adsorption of propane led to the rupture of a few C–H bonds producing propylene, which is rapidly desorbed avoiding the fission of C–C bonds. The effect of tin on selectivities has also been observed for Pt-Sn/Al_2O_3 catalysts [14].

The effect of the addition of Cl on catalytic selectivity was also observed. It is clear that dehydrogenation selectivity was higher for the Cl-free catalyst B than for the Cl-containing catalyst C (Figure 3). The latter was not only more active but also more selective for hydrogenolysis. The increase in the activity induced by Cl was due to the increment in the rate of hydrogenolysis. The presence of Cl at low Sn/Pd ratio partially cancelled the inhibiting effect of Sn on hydrogenolysis reactions. Further increase in Sn content improved the dehydrogenation selectivity even though the increase in Cl content was proportionally higher. The effect of Cl on the performance of Pd-Sn/Al_2O_3 at low Sn/Pd ratio may be due to electronic modifications of the surface Pd atoms induced by Cl, hindering some opposed electronic effect of Sn on Pd (14). At high Sn/Pd ratios, the effect of Sn was predominant. The effect of Cl on initial selectivity was rescinded by coking, as final selectivities were similar for Cl-free and Cl-containing catalysts.

Conclusions

The addition of tin did not have effect on the hydrogen adsorption capability of Pd/Al_2O_3, while the CO adsorption capability was strongly diminished. The addition of Sn along with Cl had further effect on CO chemisorption. The CO/Pd ratios were lower and independent of Sn content for the Cl-containing Pd-Sn/Al_2O_3 catalysts.

The TPR profile of the Pd/Al_2O_3 catalyst showed an intense peak at 18°C with a shoulder at 5°C, attributed to the reduction of small and large PdO particles, respectively, and two negative peaks of H_2 desorption at 61 and 85°C, which correspond to the decomposition of β-PdH phases. The addition of tin caused: (i) a diminution in size of the large PdO particles, resulting a symmetrical peak at 15°C, (ii) the appearance of a small peak at 53°C, ascribed to reduction of small fraction of SnO_2 assisted by Pd, and (iii) the formation of a single β-PdH phase giving only a negative peak at 72°C.

The initial activity of Pd/Al_2O_3 was high, but it deactivated due to coking. Coke strongly affected hydrogenolysis reactions, increasing the dehydrogenation selectivity. The addition of Sn diminished the initial activity of Pd, but increased the dehydrogenation selectivities and improved the catalytic stability.

Acknowledgements

We thank the Fondo Nacional de Ciencia, Tecnología e Innovación (FONACIT) for financial support under the Project LUZ-FONACIT S1-2002000289.

References

1. GASCÓN J., TÉLLEZ C., HERGUIDO J., MENÉNDEZ, M. ***Applied Catalysis A*** 248: 105-116, 2003.
2. BHASIN M.M., MCCAIN J.H., VORA V.M., IMAI T., PUJADÓ P.R. ***Applied Catalysis A*** 221: 397-419, 2001.
3. RODRÍGUEZ D., SÁNCHEZ J., ARTEAGA G. ***J of Molecular Catalysis*** 228: 309-317, 2005.
4. MAATMAN R., RIBBENS W., VONK, B. ***J of Catalysis*** 31: 384-388, 1973.
5. RAMOS A., HAN KIM S., CHEN P., SONG J., SOMORJAI G. ***Catalysis Letters*** 66: 5-11, 2000.
6. MASAI M., HONDA K., KUBOTA A., OHNAKA S., NISHIKAWA Y., NAKAHARA K., KISHI K., IKEDA S. ***J of Catalysis*** 50: 419-428, 1977.
7. HARO J., GÓMEZ R., FERREIRA J.M. ***J of Catalysis*** 45: 326-331, 1976.
8. SALES E., JOVE J., MENDES M., BOZON-VERDURAZ F. ***J of Catalysis*** 195: 88-95, 2000.
9. NGAMSOM B., BOGDANCHIKOVA N., AVALOS M., PRASERTHDAM P. ***Catalysis Communications*** 55: 243-248, 2004.
10. JUSZCZYK W., KARPIŇSKI Z., ŁOMOT D., PIELASZEK J., SOBCZAK J.W. ***J of Catalysis*** 151: 67-76, 1995.
11. MARÍN-ASTORGA N., PECCHI G., FIERRO J.L.G., REYES P. ***Catalysis Letters*** 91: 115-121, 2003.
12. BURCH R., URBANO F. J., ***Applied Catalysis*** 124: 121-138, 1995.
13. ARTEAGA G.J., ANDERSON J.A., BECKER S.M., ROCHESTER, C.H. ***J of Molecular Catalysis*** 145: 183-201, 1999.
14. ARTEAGA G.J., ANDERSON J.A., ROCHESTER, C.H. ***J of Catalysis*** 187: 219-229, 2000.
15. XU C., KOEL B. E. ***Surface Science***. 327: 38-46, 1995.
16. VERDIER S., DIDILLON B., MORIN S., UZIO D. ***J of Catalysis*** 218: 288-295, 2003.
17. TSUD N., SKÁLA T., ŠUTARA K., VELTRUSKÁ K., DUDR V., FABÍK S., SEDLÁÈEK L., CHÁB V., PRINCE K.C., MATOLÍN V. ***Surface Science*** 595: 138-150, 2005.
18. FERRER V., MORONTA A., SÁNCHEZ J., SOLANO R., BERNAL S., FINOL D. ***Catalysis Today*** 107: 487-492, 2005.
19. LIOTTA L.F., MARTIN G.A., DEGANELLO G. ***J of Catalysis*** 164: 322-333, 1996.
20. ZEA H., LESTER K., DATYE A.K., RIGHTOR E., GULOTTY R., WATERMAN W., SMITH M. ***Applied Catalysis A*** 282: 237-245, 2005.
21. BALDWIN T. R., BURCH R. ***Applied Catalysis A*** 66: 359-381, 1990.
22. DALEY, R.A., CHRISTOU, S.Y., EFSTATHIOU, A.M., ANDERSON, J.A. ***Applied Catalysis B*** 60: 119-129, 2005.