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Propane dehydrogenation activity of Pt and Pt–Sn catalysts supported on magnesium aluminate: influence of steam and hydrogen

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Propane dehydrogenation was carried out in hydrogen and steam as reaction media on Pt/$MgAl_2O_4$ and Pt–Sn/$MgAl_2O_4$ catalysts. A wide range of Pt and Pt–Sn concentrations was explored. Monometallic Pt catalysts were completely poisoned by steam. Concerning bimetallic Pt–Sn catalysts, tin played an important role related to the activation of platinum particles when the reaction was carried out in steam. On the other hand, tin inhibited cracking reactions leading to an increase of catalysts stability. Activation energy in hydrogen was the same for monometallic and bimetallic catalysts: 22 kcal/mol; while for the reaction in steam, values ranging from 10 to 15 kcal/mol were obtained.

Keywords: platinum, platinum–tin, magnesium aluminate spinel, propane dehydrogenation activity

1. Introduction

The new technological trends in light hydrocarbon dehydrogenation processes involve the use of promoted noble metals supported on spinel structures. The goal is to resist drastic reaction conditions handling feed streams including important quantities of steam. Water vapor seems to increase conversion by dilution; also, it diminishes coke formation by means of a water shift reaction, and contributes to regulate secondary reactions between the produced olefins [1].

From TEM particle size measurements, before and after propane dehydrogenation on Pt/$MgAl_2O_4$ catalysts, it has been reported that $MgAl_2O_4$ prevents platinum sintering [2]. When platinum is supported on zinc aluminate spinel, a strong platinum–zinc aluminate interaction, evidenced by HRTEM and hydrogen chemisorption is reported; a Pt–H complex is proposed as the active site in isobutane dehydrogenation [3]. More recently [4], bimetallic Pt–Sn catalysts supported on zinc aluminate were studied, by hydrogen interactions and isobutane dehydrogenation experiments. Concerning catalytic activity, it reaches a maximum for increasing tin concentrations. Tin addition also enhances selectivity to dehydrogenation products. TPR results showed that platinum undergoes a complete reduction, whereas tin reaches only 50% reduction [4]. The same group proposed from quantum chemistry calculations that a platinum–tin atomic orbital overlapping takes place, preventing charge transfer from platinum to tin particles avoiding hydrogen dissociation on the platinum surface [4,8].

In this work propane dehydrogenation activities of a wide range of Pt and Pt–Sn compositions supported on $MgAl_2O_4$ were explored, using hydrogen and steam as reaction media. Temperature effects are also reported.

2. Experimental

2.1. Catalysts preparation

Magnesium aluminate was prepared by coprecipitation, from the corresponding nitrates at 323 K and constant pH = 10, with a 50% v/v NH_4OH aqueous solution as coprecipitating agent; calcination was performed in two steps: 773 and 1073 K for 8 h. Detailed synthesis information can be found elsewhere [3–5]. Monometallic Pt catalysts were prepared by impregnation with increasing amounts of an alcoholic solution of $H_2PtCl_6{\cdot}H_2O$ in order to obtain final platinum loading up to 0.9 wt%. The solids were dried at 393 K for 4 h in a rotating vacuum evaporator and calcined at 823 K under dry air flow. These catalysts were labeled with numbers from 1 to 5, table 1.

The bimetallic catalysts were prepared by a double impregnation of the support: firstly with an alcoholic solution of $SnCl_2{\cdot}4H_2O$, dried at 393 K for 4 h and, finally, with an alcoholic solution of $H_2PtCl_6{\cdot}H_2O$, followed by a drying treatment at 393 K. Both drying steps were carried out in a rotatory vacuum evaporator. Calcination was performed in dry air at 823 K for 4 h. Three series of catalysts were prepared with nominal platinum loading of 0.15, 0.30 and 0.60 wt%, respectively, with tin contents ranging between 0.1 and 1.0 wt% Sn. The bimetallic catalysts can be arranged to study the effect of tin concentration over a constant amount of platinum and vice versa. These catalysts were labeled with numbers from 7 to 18, table 2.

Table 1
Propane dehydrogenation on Pt/$MgAl_2O_4$ catalysts in steam and hydrogen as reaction media. Effect of platinum concentration.[a]

Catalyst No.	Pt (wt%)	X_A (mol%)		S (mol%)		$k_d \times 10^3$ (min^{-1})	
		H_2	H_2O	H_2	H_2O	H_2	H_2O
1	0.00	0.6	2.8	57	51	–	–
2	0.23	9.8	2.0	86	84	1.13	0.78
3	0.31	12.5	2.8	86	84	0.99	2.31
4	0.50	14.1	3.3	73	75	1.33	−0.53
5	0.90	12.8	2.8	77	81	1.54	2.44

[a] $T = 823$ K, $P = 590$ Torr, C_3/(reaction medium) = 1.0 (molar ratio). τ_m = mass-time = m/v_0 = 2.08×10^{-2} g h/l. X_A = propane conversion (reaction time = 1 h) (mol%). S = propylene selectivity (reaction time = 1 h) (mol%). k_d = deactivation constant (min^{-1}).

Table 2
Propane dehydrogenation on Pt–Sn/$MgAl_2O_4$ catalysts in hydrogen and water vapor as reaction media. Effect of Pt and Sn concentration.[a]

Catalyst No.	Pt (wt%)	Sn (wt%)	X_A (mol%)		S (mol%)		$k_d \times 10^3$ (min^{-1})	
			H_2	H_2O	H_2	H_2O	H_2	H_2O
7	0.15	0.10	10.2	3.5	99	95	1.34	3.87
8	0.16	0.33	12.4	11.3	100	99	0.68	2.92
9	0.15	0.53	14.1	12.1	100	99	0.55	1.43
10	0.10	0.63	8.6	6.2	100	98	1.26	0.88
11	0.28	0.10	13.6	4.5	96	94	1.20	4.39
12	0.31	0.18	15.8	6.9	98	97	0.83	3.76
13	0.29	0.31	15.9	10.2	99	99	0.46	3.73
14	0.30	0.54	15.1	14.7	100	99	0.10	2.75
15	0.64	0.22	16.2	11.5	98	97	0.26	4.46
16	0.64	0.33	16.5	13.6	98	98	0.35	7.63
17	0.63	0.67	18.2	26.3	99	99	−0.18	1.00
18	0.68	1.06	17.4	27.5	99	100	−0.37	0.38

[a] Same conditions as in table 1.

2.2. Catalysts characterization

Chemical composition was determined by atomic absorption spectroscopy in a Perkin–Elmer 2380 apparatus. Textural properties were measured by means of nitrogen adsorption–desorption experiments (ASAP-2000, Micromeritics). The support structure was corroborated by X-ray diffraction performed on a Philips diffractometer.

Catalysts were tested in propane dehydrogenation at 823 K and 590 Torr. In all cases 0.1 g of catalyst (m) and a total flow rate (v_0) of 4.8 l/h were used. An equimolar blend of propane and water supplied by saturation or hydrogen was fed to the reactor to study the effect of different diluents. Before each reaction test, the catalysts were reduced with hydrogen (1.8 l/h) at 823 K for 1 h. The conversion of propane (X_A) is defined as the percentage of propane converted to all different products. The selectivity to propene (S) is defined as the amount of propylene obtained divided by the amount of reactive converted to all products. The main by-products observed were methane, ethane and ethylene. To describe deactivation curves, an overall parallel deactivation mechanism was assumed. In most cases, the propane reaction was carried out with a low conversion; under this condition, the reactor behaves as mix flow. Based on the first order for deactivation and the surface reaction kinetics, the following model can be derived:

$$\ln\frac{1-X_A}{X_A} = k_d t + \ln\frac{1-X_{A_0}}{X_{A_0}},$$

from which the deactivation constants (k_d) were obtained [7].

3. Results and discussion

3.1. Support

Due to the pH of the synthesis and the coprecipitating agent employed [5], the obtained material support was rich in aluminum with respect to the stoichiometric amount (Al/Mg = 2.3). This will contribute to avoiding Pt–Mg interactions, similar to the reported for the platinum–zinc aluminate system [9].

XRD diffraction patterns correspond to a magnesium spinel structure (JCPDS card-21 1152). The broad diffraction peaks at lower calcination temperature indicate low crystal definition; at higher calcination temperature (1373 K), narrower diffraction peaks are obtained showing an increment in crystallite size [5]. Free aluminum or magnesium phases were not detected, although aluminum is present 15 wt% in excess related to the stoichiometric amount to form magnesium aluminate, indicating its possible incorporation into the spinel structure.

Support textural properties were: surface area, 103 m^2/g; pore volume, 0.2 cm^3/g; average pore diameter, 82 Å. This material was used as a support in the preparation of all the catalysts.

3.2. Monometallic Pt/$MgAl_2O_4$ catalysts

Table 1 shows conversion, selectivity and deactivation constants using hydrogen and steam as diluents for the $MgAl_2O_4$ support and for Pt/$MgAl_2O_4$ catalysts, with platinum concentrations ranging from 0.23 to 0.9 wt%. The monometallic catalysts did not show any catalytic activity when steam is the reaction medium for all Pt concentrations studied. The observed propane conversions, measured in the first hour of reaction time, were similar to that obtained for the support, even though the selectivity of platinum catalysts was higher. When steam is used, $MgAl_2O_4$ increases its catalytic activity, but propane conversion remains very low. The increasing activity values are probably due to dilution effects.

Propylene selectivity decreases with increasing platinum contents; this tendency is confirmed by means of a 1.35 wt% Pt catalyst in hydrogen as the reaction medium. In this case the selectivity measured at 823 K was 53%, which is very similar to the value obtained for the support (57%). The reaction media (hydrogen or steam) do not affect the propylene selectivity. At this point, it seems that steam blocks platinum dehydrogenation sites without any influence on the cracking properties of platinum particles. Deactivation constants are similar in both reaction media, and poorly affected by platinum concentration.

3.3. Bimetallic Pt–Sn/$MgAl_2O_4$ catalysts

Table 2 shows conversion, selectivity and deactivation constants in hydrogen and steam as diluents for the bimetallic Pt–Sn/$MgAl_2O_4$ catalysts. Tin addition significantly increased the propylene selectivity in all the catalysts (~100%) in both reaction media. Tin inhibits cracking properties of platinum particles. It is worth to note that tin plays an important role in platinum activation when steam is used as the reaction medium; the reaction is better performed in steam when metal loading is relatively high (0.6 wt% of both metals). Tin modifies the Pt–H_2O interaction, because water does not poison the bimetallic Pt–Sn catalysts as it does monometallic platinum catalysts.

When hydrogen is the reaction medium, conversion is proportional to metal concentration up to 0.3 wt% of both metals; for higher metal concentrations, propane conversion remains almost constant, which might be indicative of an equilibrium limitation. Figure 1 shows values from table 1 and a selection from table 2 to illustrate the above described behavior: figure 1(a) for hydrogen operation and figure 1(b) for the reaction in steam. The following catalyst numbers were selected to integrate figure 1 (a) and (b): Pt/$MgAl_2O_4$ catalysts were taken from table 1, catalysts Nos. 1–5. The Pt–Sn/$MgAl_2O_4$ catalysts were taken from table 2, the 0.3% Sn catalysts are the Nos. 8, 13, 16 and the 0.6% Sn series corresponds to Nos. 10, 14 and 17. With this arrangement it is possible to see the effect of platinum concentration on a constant amount of tin.

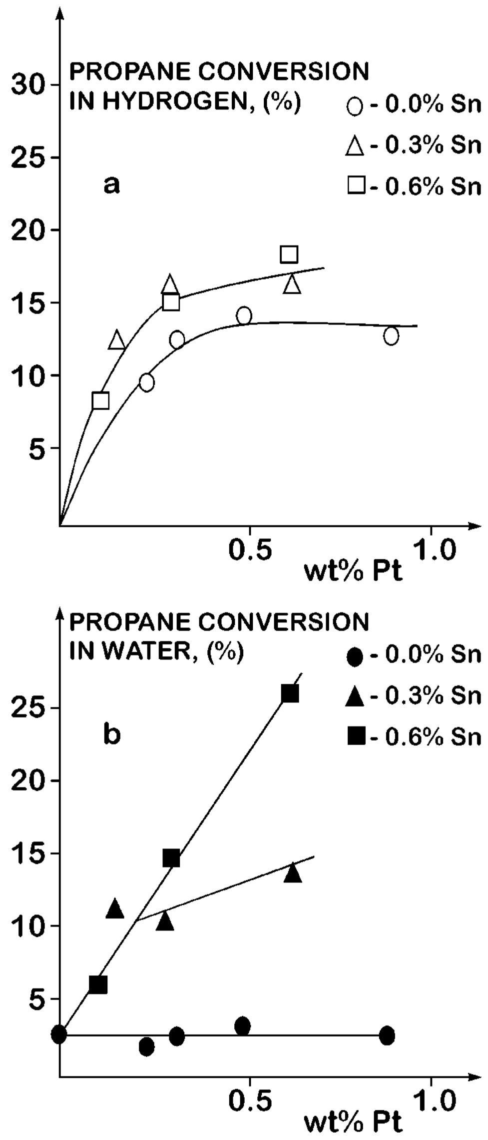

Figure 1. Propane dehydrogenation on Pt and Pt–Sn catalysts supported on magnesium aluminate, in hydrogen (a), and in steam (b) as reaction media: effect of Pt and Pt–Sn concentration on propane conversion.

Taking into account our experimental results, it is possible to recommend high metallic concentrations (0.6–0.7 wt% of both metals) when the reaction is carried out in steam, and lower metallic contents (0.3–0.4 wt% of both metals) when the reaction takes place in hydrogen.

Concerning catalysts deactivation, it is evident that the deactivation constants (k_d) decrease with increasing tin concentration in all the Pt–Sn series. The higher values of deactivation constants are found when reaction takes place in steam ($k_d \approx 4.0 \times 10^{-3}$ min^{-1}) with low tin contents; when tin concentration is high enough, similar deactivation

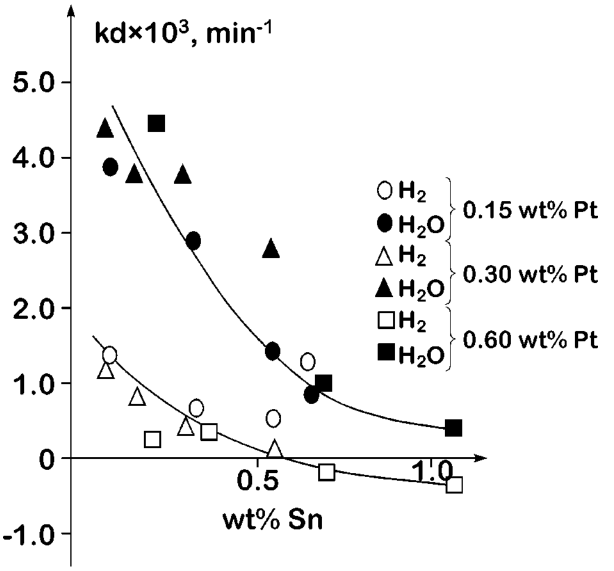

Figure 2. Propane dehydrogenation on Pt–Sn catalysts supported on magnesium aluminate, in hydrogen and in water vapor as reaction media: effect of Pt–Sn concentration on deactivation constant (k_d).

Table 3

Propane dehydrogenation in hydrogen or water vapor as reaction media on a 0.5 wt% Pt/$MgAl_2O_4$ (Pt) and on a 0.45 wt% Pt–0.42 wt% Sn/$MgAl_2O_4$ (Pt–Sn) catalyst. Effect of temperature on propane conversion.[a]

T (K)	X_A (mol%)			
	Pt		Pt–Sn	
	H_2	H_2O	H_2	H_2O
763	4.5	1.5	6.1	11.2
783	6.8	1.7	8.1	10.8
803	8.0	1.9	12.2	12.4
823	12.7	3.3	17.0	18.4

[a] Same conditions as in table 1.

constants are obtained ($k_d \approx 1.0 \times 10^{-3}$ min^{-1}) in both reaction media. Negative deactivation constants are obtained when catalyst activity goes from low to higher values; this is probably due to an increasing platinum dispersion while the reaction is carried out. Figure 2 displays the overall tendency of k_d values with respect to tin concentration of bimetallic Pt–Sn catalysts.

3.4. Temperature effects

Reaction temperature was explored between 763 and 823 K, with a monometallic 0.5 wt% Pt catalyst (Pt) and a bimetallic 0.45 wt% Pt–0.42 wt% Sn catalyst (Pt–Sn). Also, hydrogen and steam were used as reaction media; the results obtained are shown in table 3. In order to estimate activation energy values, a first-order surface reaction was assumed to calculate rate constants; figure 3 shows an Arrhenius plot of the results.

When hydrogen is the reaction medium, the linear form of the Arrhenius law perfectly fits; bimetallic Pt–Sn catalysts were always more active than monometallic Pt catalyst, the activation energy in both cases being the same: 22 kcal/mol.

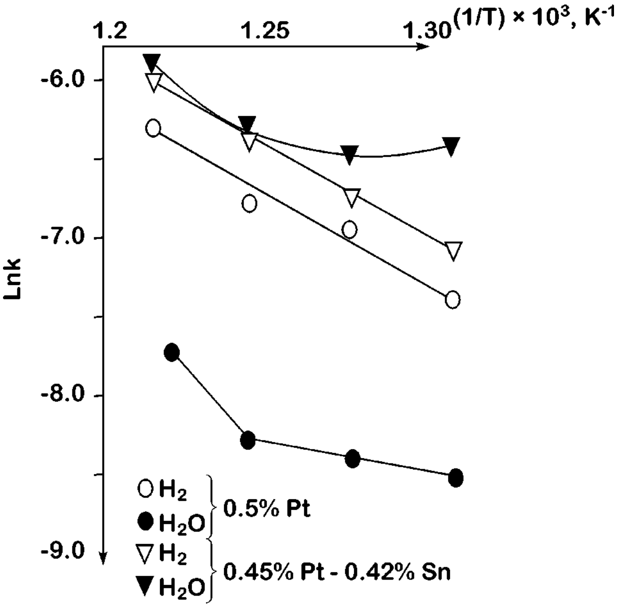

Figure 3. Propane dehydrogenation on a monometallic 0.5 wt% Pt and on a bimetallic 0.45 wt% Pt–0.42 wt% Sn catalyst supported on magnesium aluminate, in hydrogen and in water vapor as reaction media: effect of temperature on reaction rate.

Table 4

Propane dehydrogenation in hydrogen or water vapor as reaction media on a 0.5 wt% Pt/$MgAl_2O_4$ (Pt) and on a 0.45 wt% Pt–0.42 wt% Sn/$MgAl_2O_4$ (Pt–Sn) catalyst. Effect of temperature on propylene selectivity.[a]

T (K)	S (mol%)			
	Pt		Pt–Sn	
	H_2	H_2O	H_2	H_2O
763	93	92	100	100
783	93	65	99	100
803	92	86	94	99
823	89	74	99	98

[a] Same conditions as in table 1.

When the reaction is carried out in steam, the observed behaviors do not follow the Arrhenius linear function; the reaction rate at low temperatures is lower than the value predicted from an Arrhenius linear plot. The low activity of the catalysts in water steam is confirmed. For the reasons mentioned above, the activation energies in water were less accurately computed; taking into account the values given by the linear regression of all the points, the activation energy obtained for the monometallic Pt catalyst was 15 kcal/mol, while for the bimetallic Pt–Sn catalyst it was 11 kcal/mol. The deviations from the Arrhenius law for water operation are probably due to propane diffusion effects through the gas phase near the catalyst surface and a strong chemical interaction between water molecules and Pt particles takes place, which is supported by the fact that water poisons the activity of monometallic Pt particles. This significantly impacts on the adsorption of propane on the catalyst surface and thus the activity.

Propylene selectivity obtained for bimetallic Pt–Sn catalysts was very near to 100% at all temperatures and reaction media studied. Monometallic Pt catalyst showed a lower selectivity and higher sensitivity to temperature changes when steam is present.

Concerning monometallic Pt/$MgAl_2O_4$ catalysts, it is evident that platinum–water interaction is stronger than platinum–propane interaction, because water dislodges propane from the platinum surface, which implies that support hydrophobicity is not the key requirement to reach catalytic performance in water as the reaction medium. Dehydrogenation active sites are poisoned by water molecules without affecting cracking sites, because selectivity is almost the same in both reaction media studied.

With respect to bimetallic Pt–Sn/$MgAl_2O_4$ catalysts, it can be stated that tin, even in very low concentrations, clearly modifies the catalytic properties of platinum. An attempt to explain the points stated above, is to consider that tin promotes weaker hydrocarbon–platinum bonds. To explain this phenomenon, in a previous work [4,8], on the basis of quantum chemistry calculations, a charge transfer from atomic orbitals of platinum to atomic orbitals of tin has been proposed; this charge transfer mainly weakens the interaction of platinum with hydrogen or hydrogen-containing molecules. In this case, for increasing tin concentrations, catalytic activity does not reach a clear maximum as it does when the same metals are supported on alumina [10] or zinc aluminate [4]. This would imply that magnesium aluminate promotes a different Pt–Sn interaction.

4. Conclusions

The main conclusions of the promotional effect of tin over platinum supported on magnesium aluminate can be summarized as follows:

(a) Tin suppressed cracking properties of platinum particles, and strongly improved the dehydrogenation selectivity.

(b) Compared with steam, when H_2 is used as the reaction medium, dehydrogenation reactions reached higher conversions with relative low deactivation constants on both series of Pt and Pt–Sn catalysts, except for the higher metallic concentrations.

(c) Tin improved the activity of Pt/$MgAl_2O_4$ catalysts when steam is the reaction medium. The monometallic Pt catalysts were inactive in steam.

(d) With increasing tin concentrations, lower deactivation constants were obtained, probably due to the elimination of cracking reactions.

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References

[1] S.R. Vatcha, F. Trifirò and F. Cavani, in: *Oxidative Dehydrogenation and Alternative Dehydrogenation Processes*, Catalytica No. 4992 OD, ed. D. Helius (1993).

[2] R.J. Rennard and J. Freel, J. Catal. 98 (1986) 235.

[3] G. Aguilar-Ríos, M.A. Valenzuela, H. Armendáriz, P. Salas, J.M. Dominguez, D.R. Acosta and I. Schifter, Appl. Catal. A 90 (1992) 35.

[4] G. Aguilar-Ríos, M.A. Valenzuela, P. Salas, H. Armendáriz, P. Bosch, G. Del Toro, R. Silva, V. Bertín, S. Castillo, A. Ramirez-Solis and I. Schifter, Appl. Catal. 127 (1995) 65.

[5] J. Salmones, J.A. Galicia, O. Martínez, M.A. Valenzuela and G. Aguilar-Ríos, in: *Acta XVI Simp. Iberoam. Catal.*, Vol. 1 (1998) pp. 277, 282.

[6] O.A. Borias, A. Holmen and E.A. Blekkan, J. Catal. 158 (1996) 1.

[7] O. Levenspiel, *Chemical Reaction Engineering*, 2nd Ed. (Wiley, New York, 1972) p. 537.

[8] S. Castillo, E. Poulain, V. Bertin and A. Cruz, Int. J. Quantum Chem. 29 (1995) 207.

[9] N.A. Pakhomov, R.A. Buyanov, E.M. Moroz, G.R. Kotelnikov and V.A. Patamov, React. Kinet. Catal. Lett. 9 (1978) 257.

[10] B.H. Davis, Stud. Surf. Sci. Catal. 75 (1993) 889.