

## Effect of barium and lanthanum oxides on the properties of Pt/KL catalysts in the n-heptane dehydrocyclization

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Six fractions of zeolite KL were impregnated with 1, 3 and 5 wt% of Ba or La, respectively, with nitrate precursors aqueous solutions. After calcination at 873 K to form BaO or La<sub>2</sub>O<sub>3</sub>, 1 wt% of Pt was incorporated to the supports by the impregnation method. Metal dispersion decreases as the Ba concentration increases, but it is not substantially affected by the La addition. The CO/FTIR and the competitive hydrogenation of benzene + toluene results indicate that an electron enrichment of the Pt particles occurs by effect of the additives. The increase of the electron density of the Pt in Ba-catalysts is higher than for the La-catalysts. Moreover, the Ba addition highly enhances the aromatization and terminal hydrogenolysis activities, without substantial modification of the yields to the other reaction products. The yield to toluene is also increased by effect of 1 wt% of La, but it does not increase with the La concentration. The TEM-EDX studies indicate that the different distribution of the BaO and La<sub>2</sub>O<sub>3</sub> in the zeolite may be the origin of the different surface and catalytic effects of these oxides in the Pt/KL catalysts.

### 1. INTRODUCTION

It is well known that Pt/KL catalysts exhibit a high selectivity to transform light n-paraffines (C<sub>6</sub> and C<sub>7</sub>) into aromatic hydrocarbons [1]. This unique selectivity is frequently attributed to the platinum clusters located in a non-acidic environment in the cavities of the zeolite L [2]. In other cases [3] it is proposed that the aromatization specificity of Pt/KL is essentially due to the singular structure of the zeolite L, which orientates the paraffin molecule in the linear channels in such a way that it favors the terminal C-adsorption and the C<sub>1</sub>-C<sub>6</sub> ring closure on the Pt sites, leading to increased corresponding aromatic hydrocarbon formation. Following to Iglesia et al. [4], however, the aromatizing activity is a specific function of the unpoisoned platinum surfaces, no matter which the support is.

Most of the researches carried out in the past have been devoted to the n-hexane aromatization [5], while those concerning to n-heptane are more scarce, in spite of the presumable growth of the demand of toluene as a possible substitute of benzene and xylenes in the reformulated gasoline. In a previous work [6] it was reported that the incorporation of Ba<sup>2+</sup> to the zeolite L by ion-exchange does not substantially modify either the physicochemical properties or the aromatization activity of a Pt/KL catalyst. The partial exchange of K<sup>+</sup> by La<sup>3+</sup>, on the other hand, highly decreases the

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electron density of Pt particles, inhibits the aromatization and promotes the acid activity of the catalyst. In the present work the effect of the bases BaO and La<sub>2</sub>O<sub>3</sub> on the performances of a Pt/KL catalyst in the n-heptane dehydrocyclization is analyzed. The catalysts were characterized by TPR, gas chemisorption, CO/FTIR, competitive hydrogenation of toluene + benzene mixtures and TEM-EDX. The catalytic performances are explained from the electronic state of the platinum clusters.

## 2. EXPERIMENTAL

### 2.1. Catalyst preparation

Several portions of a commercial zeolite KL (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 6.0), calcined at 873 K, were impregnated by incipient wetness technique with barium nitrate or lanthanum nitrate aqueous solutions in an adequate concentration to obtain 1, 3 or 5 wt% of Ba or La. After calcination at 873 K the Pt (1 wt%) was loaded following analogous procedure and using Pt(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub> as precursor. The catalysts were calcined at 573 K in a O<sub>2</sub> stream for 3 h and then reduced at 773 K under H<sub>2</sub> flow, for 3 h. In these conditions, TPR measurements showed that the catalysts were completely reduced.

### 2.2 Catalyst characterization

The reducibility of the catalysts was determined by Temperature Programmed Reduction (TPR) in a flow system with thermal conductivity detector. The TPR profiles were registered heating the calcined precursors at 15 K min<sup>-1</sup> from room temperature to 823 K under 30 mL min<sup>-1</sup> of 5% H<sub>2</sub>/Ar.

The number of surface platinum atoms ( $P_{ts}$ ) was measured by the H<sub>2</sub>-O<sub>2</sub> titration method [6] in a dynamic system at room temperature. Pulses of H<sub>2</sub> (50 μL) were used to titrate the O<sub>2</sub> previously adsorbed on the reduced catalyst. From the volume of H<sub>2</sub> uptake ( $H_{up}$ ) the number of surface platinum atoms was calculated assuming an atomic stoichiometry  $H_{up}/P_{ts} = 3/1$ . Platinum dispersion ( $D$ ) is defined as  $D = P_{ts}/P_t$ , in where  $P_t$  is the number of platinum atom per gram of catalyst determined by chemical analysis.

The electronic state of the platinum was studied by FTIR, using CO as probe molecule. The FTIR spectra were recorded at room temperature in the range 4800 - 400 cm<sup>-1</sup>. The self-supported wafers were previously contacted with 4 kPa of CO for 5 min. The electronic state of Pt was also evaluated by competitive hydrogenation of toluene + benzene mixtures. The reaction was performed in a conventional flow reactor unit at 373 K and atmospheric pressure. The toluene pressure was changed in the range 1.9 - 9.6 kPa, while those of benzene (2.0 kPa) and hydrogen (65.8 kPa) were maintained constant, using nitrogen to balance. From the kinetic measurements and following the method proposed by Phoung et al. [7] the ratio of toluene to benzene adsorption coefficients ( $K_{TB}$ ) was calculated. Prior to the characterization measurements the catalyst samples were outgassed in situ at 573 K, under flow of Argon.

Transmission Electron Microscopy with Energy Dispersive X-ray was also utilized to obtain complementary data about the distribution of the components of the catalyst in the support.

### 2.3 Catalytic activity measurements

The n-heptane dehydrocyclization was carried out in a fixed-bed tubular reactor containing 2 g of catalyst (particle size 0.6 - 1 mm) at 698 K, 100 kPa, H<sub>2</sub>/nC<sub>7</sub>H<sub>16</sub> = 7.3 mole/mole and LHSV = 3.42 h<sup>-1</sup>. In these conditions neither internal nor external diffusion limitations are present. The

reactor was heated under  $H_2$  flow up to the reaction temperature. Once the system was stabilized the n-heptane was fed and the reactor effluent periodically collected and analyzed by Gas Chromatography. All the reactant gases were successively passed through a Deoxo purifier and a 5A molecular sieve filter. Catalysts were evaluated from the composition of the samples collected after 30 min on stream.

## RESULTS AND DISCUSSION

### 3.1. Characterization

The results of characterization of the catalysts are given in Table 1. Dispersion of Pt decreases when the BaO increases, whereas it practically remains unchanged with the  $La_2O_3$  concentration.

Table 1  
Characterization of the catalysts

Catalyst	<i>Me</i> (wt%)	Pt loaded (wt%)	<i>D</i> (%)	<i>I/I</i> <sub>0</sub>				<i>K</i> <sub>TB</sub>
				2120*	2034*	1997*	1963*	
CKPt	0	0.98	42	0.21	0.85	0.60	0.32	1.88
CBaPt1	0.98	0.99	40	0.10	1.14	1.03	0.71	1.09
CBaPt3	2.87	0.97	34	0.06	1.13	1.16	0.91	0.93
CBaPt5	4.81	1.02	24	0.05	1.13	1.17	1.00	0.77
CLaPt1	0.96	0.98	41	0.07	0.67	0.61	0.46	1.12
CLaPt3	2.94	0.99	44	0.07	0.81	0.78	0.68	1.06
CLaPt5	4.72	0.98	43	0.06	0.82	0.82	0.76	1.07

*Me*, Ba or La; *D*, dispersion; *I/I*<sub>0</sub>, relative intensity of IR bands; \* wavenumber,  $cm^{-1}$ ; *K*<sub>TB</sub>, ratio of toluene to benzene adsorption coefficients.

The FTIR spectra of the adsorbed CO on CBaPt and CLaPt catalysts are given in Figs. 1 and 2, respectively. The spectrum of CKPt exhibits a broad band in the range 2150 - 880  $cm^{-1}$ , with four maxima at 2073, 2060, 2034 and 1997  $cm^{-1}$  and two shoulders at 2120 and 1963  $cm^{-1}$  corresponding to CO linearly bonded to Pt species in different electronic states [8]. The band at 2073 is associated to CO adsorbed on  $Pt^0$ , while the other bands at lower wavenumbers can be attributed to electron enriched platinum, probably located inside the cavities of the zeolite. The band at 2120  $cm^{-1}$  denotes the presence of electron-deficient metal atoms [6,10].

As shown in Fig. 1, the IR spectrum of CKPt is strongly modified by the presence of BaO. Taking as reference the band at 2073  $cm^{-1}$  the relative intensity values (*I/I*<sub>0</sub>) calculated by deconvolution of the spectra are summarized in Table 1. The *I/I*<sub>0</sub> values at wavenumbers lower than 2000  $cm^{-1}$  increase as the BaO content increases, while that of the band at 2120  $cm^{-1}$  decreases. These results indicate that an electron enrichment of the Pt particles in the zeolite occurs by effect of BaO addition. Assuming that the *K*<sub>TB</sub> is a kinetic measure of the acidity of the catalyst, as it was proposed by Larsen and Haller [9], the FTIR results are consistent with the values of *K*<sub>TB</sub> which decrease as BaO concentration increases.

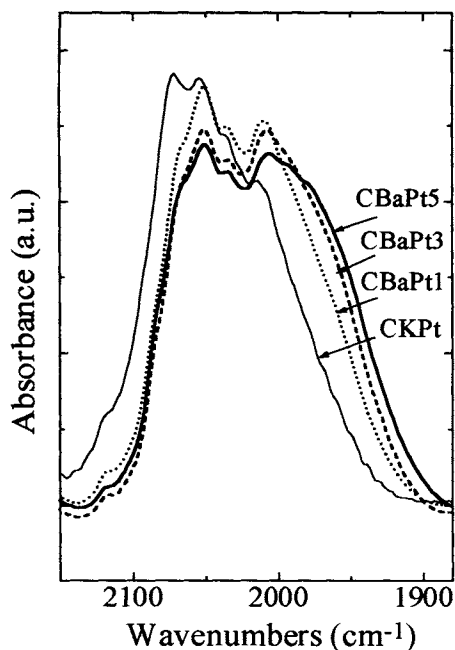


Fig. 1. FTIR spectra of CO adsorbed on CBaPt catalysts.

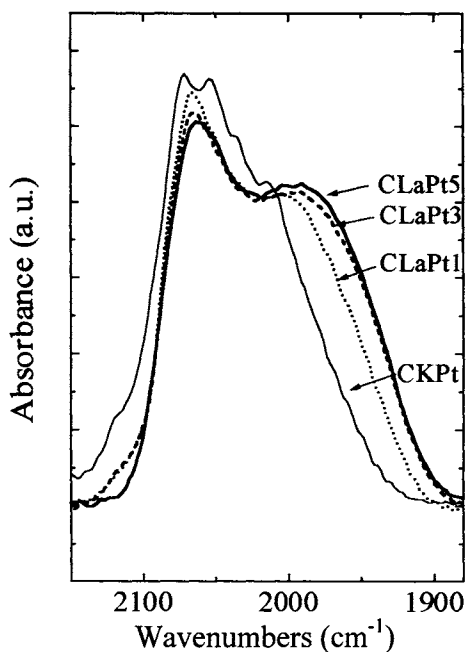


Fig. 2. FTIR spectra of CO adsorbed on CLaPt catalysts.

From the IR spectrum of the catalyst containing 1 wt% La a similar conclusion can be drawn, but the  $I/I_0$  values indicate that the increase of the electron enrichment of the platinum atoms in samples with 3 and 5 wt% of lanthanum is lower than for Ba catalysts. Changes observed in the dispersion and  $K_{T/B}$  values for CBaPt and CLaPt catalysts are parallel to those of CO/FTIR spectra, thus suggesting that some qualitative, in addition to quantitative, difference between the effect of BaO and  $\text{La}_2\text{O}_3$  takes place. It seems that the extent of  $\text{Pt} \leftrightarrow \text{BaO}$  interaction is higher than the  $\text{Pt} \leftrightarrow \text{La}_2\text{O}_3$  one.

### 3.2. Dehydrocyclization activity

The performances of the catalysts in the hydroconversion of n-heptane at 698 K are summarized in Table 2. Since the activity decays with the time on stream, the tabulated values were calculated from the composition of the product collected after 30 min of reaction. Conversion of n-heptane ( $X$ ) is the molar percentage of n-heptane fed to the reactor transformed into products. The yield to a product  $i$  ( $Y_i$ ) is the number of n-heptane molecules transformed into a product  $i$  per 100 molecules of n-heptane fed to the reactor. The selectivity toward toluene ( $S_{\text{tol}}$ ) is defined as the number of n-heptane molecules transformed into toluene per 100 molecules of n-heptane converted. From the number of platinum surface atoms ( $Pt_s$ ) and the conversion values the turnover frequency ( $TOF$ ) is calculated as the number of n-heptane molecules transformed per

exposed platinum atom per second. The fraction C<sub>2</sub>–C<sub>7</sub> includes: n-paraffines C<sub>2</sub>–C<sub>6</sub>, branched paraffines C<sub>4</sub>–C<sub>6</sub>, heptane isomers and cycloalkanes C<sub>5</sub> and C<sub>6</sub>.

The addition of 1 wt% of Ba or La strongly improves the yields to toluene, benzene and methane and no appreciable modification of the yields to the other products takes place. As a consequence, the toluene selectivity ( $S_{Tol}$ ) highly increases. Additionally, an increase of the total  $TOF$  is observed. A parallelism between the cyclization (toluene + benzene) and terminal hydrogenolysis (methane) activities does exist, as it was also found by other workers [4]. When the concentration of BaO increases a significant enhancement of the yield to toluene is observed. These results indicate that BaO specifically improves the aromatization activity of the Pt/KL catalyst. This effect is probably due to the increase of the surrounding basicity of the Pt sites located in the cavities of the zeolite L. This parallelism can be explained if one accepts that both catalytic functions are a property of the Pt sites of high electron density. The electronic enrichment of the Pt atoms in samples containing BaO and in that with 1 wt% La, evidenced by FTIR and  $K_{TB}$ , reasonably supports this hypothesis.

Table 2

Dehydrocyclization activity of the catalysts

T = 698 K; H<sub>2</sub>/nC<sub>7</sub> = 7.3 mol/mol; WHSV = 3.42 h<sup>-1</sup> y P = 100 kPa.

Catalyst	CKPt	CBaPt1	CBaPt2	CBaPt3	CLaPt1	CLaPt3	CLaPt5
<sup>a</sup> Me (wt%)	0	1	3	5	1	3	5
X (%)	14.9	29.5	40.2	46.0	26.5	24.7	23.2
10 <sup>3</sup> TOF (s <sup>-1</sup> )	65.6	136.6	218.6	334.0	119.4	106.1	95.1
Y <sub>Tol</sub> (%)	5.1	16.2	4.5	30.6	2.2	11.6	10.9
Y <sub>Bz</sub> (%)	0.3	1.8	2.2	2.3	1.4	1.3	1.1
Y <sub>C2-C7</sub> (%)	9.1	9.8	11.6	11.8	11.0	0.4	9.9
Y <sub>Cl</sub> (%)	0.4	1.8	1.8	1.8	1.9	1.6	1.2
10 <sup>3</sup> TOF <sub>Tol+Bz</sub> (s <sup>-1</sup> )	23.6	83.5	144.7	237.1	61.1	55.4	49.1
S <sub>Tol+Bz</sub> (%)	36.0	61.1	66.4	71.0	51.2	52.2	51.7

<sup>a</sup>nominal Ba or La content; X, conversion; TOF, turnover frequency; Y, yield; S, selectivity.

Unexpected results were obtained with the samples CLaPt3 and CLaPt5. In fact, the performances of these catalysts do not practically change or slightly decrease with respect to those of CLaPt1, despite of the fact that La<sub>2</sub>O<sub>3</sub> is a strong base. In an attempt to explain this anomalous behavior, catalysts were analyzed by TEM-EDX. The results showed that in Ba-samples the surface is homogeneously covered by both BaO and Pt particles in a close vicinity. In CLaPt3 and CLaPt5 catalysts, however, most of the La<sub>2</sub>O<sub>3</sub> and Pt particles appear clearly segregated. Since a uniform distribution of both components of the catalysts is required for a good interaction between Pt and BaO or La<sub>2</sub>O<sub>3</sub>, the different distribution of the BaO and La<sub>2</sub>O<sub>3</sub> particles in the zeolite is probably the origin of the different surface and catalytic properties of both type of catalysts.

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#### REFERENCES

1. J.R. Bernard, Proc. 5th Int. Conf. Zeolites, L.V. Rees (Ed) Heyden, London, 1980, p.686.
2. C. Besoukhanova, J. Guidot, D. Barthomeuf, M. Breyse and J.R. Bernard, J. Chem. Soc. Faraday Trans., 77, No 1 (1981) 1595.
3. S.J. Tauster and J.J. Steger, J. Catal., 125 (1990) 387.
4. E. Iglesia and J.E. Baumgartner, Stud. Surf. Sci. Catal., 75 (1993) 993.
5. P. Mériaudeau and C. Naccache, Catal. Rev.-Sci. Eng., 39 (18-2) (1997) 5.
6. M. Grau, L. Daza, X.L. Seoane and A. Arcoya, Catal. Lett., 53 (1998) 161.
7. T.T. Phuong, J. Massardier and P. Gallezot, J. Catal., 102 (1986) 456.
8. A. Yu Stakheev, E.S. Shpiro, N.I. Jaeger and G. Schulz-Ekloff, Catal.Lett., 34 (1995) 293.
9. G. Larsen and G.L. Haller, Catal. Lett., 3 (1989) 103.
10. W. Juszczyk, Z. Karpinski, I. Ratajczykowa, Z. Stanasiuk, J. Zielinski, L.L. Sheu and W.M.H. Sachtler, J. Catal., 120 (1989) 68.