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Surface characterization and dehydrocyclization activity of Pt/KL catalysts prepared by different methods

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Abstract

Three Pt/KL-zeolite catalysts containing 1 wt.% of metal were prepared by different procedures: CI-1 and CI-2 by wetness impregnation of the zeolite with aqueous solutions of $Pt(NH_3)_4(OH)_2$ and $Pt(NH_3)_4(NO_3)_2$, respectively, and CE-3 by ion exchange with a $Pt(NH_3)_4(OH)_2$ solution. These samples were successively calcined at 573 K and reduced at 773 K. An additional sample, CE-3-n, was obtained from CE-3 by ion-exchange with KNO_3. The catalysts were characterized by H_2–O_2 titration, TPD of NH_3, XRD, CO–FTIR and XPS and tested in the dehydrocyclization of *n*-heptane to toluene at 723 K, 100 kPa, WHSV $= 3.4\ h^{-1}$ and $H_2/nC_7 = 7.3\ mol\ mol^{-1}$ in a fixed bed tubular reactor. Characterization results show that Pt dispersion for the ion exchanged samples is higher than for the impregnated ones and CE-3 is the more acidic catalyst. FTIR measurements indicate that the highest population of electron reach platinum species ($Pt^{\delta-}$) is found in CE-3-n, while CE-3 exhibits the highest concentration of electron deficient platinum species ($Pt^{\delta+}$). The order of dehydrocyclization activity, CE-3-n $>$ CI-2 $>$ CI-1 $>$ CE-3, roughly correlates with that of the intensity of the FTIR bands attributed to $Pt^{\delta-}$. The low selectivity toward toluene of CE-3 is attributed to the protons generated during the reduction of Pt^{2+} exchanged.

Keywords: FTIR; XPS; Pt/KL catalysts; Dehydrocyclization; Toluene

1. Introduction

To improve our atmosphere and reduce the fuel pollution the concept of reformulated gasoline was introduced in the automotive sector (US Clear Act Amendment of 1990), which includes the reduction of the aromatics content below 25%. In this gasoline, benzene is limited to 1 wt.%, due to its cancerous character, while the proportion of xylenes and other aromatics C_9–C_{10} have to be substantially reduced due to their photochemical activity. In contrast, toluene does not present these disadvantages and, since it has a high RON + MON, it could substitute for the other aromatics in the reformulated gasoline. Should this be the case, the toluene demand would exceed the amount produced by the conventional catalytic processing of naphtha reforming. For this reason it is necessary to develop new preparation methods more productive than the preceding one. A procedure with a good prospect is the dehydrocyclization of *n*-heptane with Pt/KL catalysts, which are highly active and selective in the aromatization of *n*-hexane [1–3].

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The unique dehydrocyclization activity of Pt/KL has been attributed, among others, to: (a) the singular structure of the KL zeolite [4]; (b) the high aromatization activity of electron rich Pt particles inside the zeolite [5,6] and (c) the capability of the zeolite to prevent agglomeration and carbon fouling of the Pt particles within the channels [7]. More recently, it has been proposed that the high aromatizing selectivity of Pt/KL is the result of some combination effects such as: size of the Pt clusters, basicity of the zeolite and constrictions imposed by the support pores [8]. Although these physicochemical properties are characteristic of the Pt/KL system, they can be affected by the nature of the components and the preparation method of the catalyst. With this idea in mind, we have prepared in this work several Pt/KL samples using either $Pt(NH_3)_4(OH)_2$ or $Pt(NH_3)_4(NO_3)_2$ as Pt precursor, following different methods. The catalysts were characterized by FTIR, XPS, XRD and H_2–O_2 titration and their catalytic activity was evaluated in the dehydrocyclization of *n*-heptane to toluene. The catalytic performance is explained from the electronic state of Pt particles and their location in the zeolite.

2. Experimental

2.1. Catalysts preparation

Three catalysts containing 1 wt.% of Pt were prepared using as support a KL zeolite (Union Carbide, SK-45, Si/Al = 3 atom/atom, 0.6–1 mm particle size) previously calcined at 873 K. The preparation procedure was as follows:

Sample CI-1: Pt was incorporated by incipient wetness impregnation from a $Pt(NH_3)_4(OH)_2$ aqueous solution.

Sample CI-2: Prepared as CI-1, but using $Pt(NH_3)_4(NO_3)_2$ as precursor.

Sample CE-3: The metal was incorporated by ion exchange. A $Pt(NH_3)_4(OH)_2$ aqueous solution was added dropwise to an aqueous suspension of 30 g zeolite and 500 ml of distilled water, under stirring at 333 K. After 24 h at reflux temperature, the slurry was filtered and washed with distilled water to remove occluded ions. The powder was pelleted and crushed to 0.6–1 mm particle.

After drying at 393 K for 16 h, all the samples were calcined under flow of O_2 at 573 K and then reduced in hydrogen stream (500 ml h^{-1} $g_{cat}{}^{-1}$) at 773 K for 3 h. The heating rate was 2 K min^{-1}.

In order to remove the acid sites of CE-3, a portion of this sample was exchanged with a 0.3 M KNO_3 solution for 60 h at 303 K. The solid, washed and dried, was heated at 373 K for 12 h in a stream of H_2. This sample was labeled as CE-3-n.

2.2. Catalyst characterization

Metal dispersion was defined as $D = 100\ Pt_S/Pt_T$ and calculated from the number of exposed Pt atoms per gram of catalyst (Pt_S) measured by H_2–O_2 titration and the total Pt atoms per gram (Pt_T) determined by inductive coupled plasma. The H_2–O_2 titration measurements were carried out in a dynamic system at RT. The catalyst samples (0.5 g) were treated at 723 K under hydrogen stream for 30 min. After evacuation at 573 K for 1 h and cooling to RT, pulses of O_2 (50 μl) were introduced in the carrier gas until total saturation of the metal surface. The adsorbed oxygen was titrated introducing pulses of hydrogen and Pt_S calculated assuming a molar stoichiometry $H_2/Pt_S = 1.5/1$. From D values, the average particle size (d) was calculated assuming a cubic model for the Pt particles.

Surface acidity of the catalysts (A) was determined by temperature programmed desorption (TPD) of NH_3 in a flow system with thermal conductivity detector. The outgassed catalyst sample (0.5 g) was saturated with pulses (1 ml) of NH_3 at room temperature (RT) and then stabilized at 373 K in He stream to remove the physisorbed NH_3. After cooling, the sample was heated from RT to 823 K at 10 K min^{-1} and the desorbed NH_3 collected with a 0.01 M HCl solution.

Crystallinity of the catalysts was checked by X-ray diffraction in a Seifert C-3000 powder diffractometer, using Cu Kα radiation at 40 mA and 40 kV, with slits of 1, 0.1°.

The *chemical state* of Pt was studied by FTIR using CO as probe molecule. The spectra were registered in a Nicolet 5ZDX spectrometer at RT in the range 2200–1400 cm^{-1} with a resolution of 4 cm^{-1}. The self supported wafer of catalyst was successively pretreated in a stream of H_2 at 723 K for 30 min, outgassed at

10^{-3} Pa at the same temperature for 1 h. After cooling to room temperature the IR spectrum was recorded and then the sample contacted with 2 kPa of CO for 5 min prior to recording a new spectrum. The spectrum of chemisorbed CO was obtained by subtraction of those spectra. The number and position of the band components of the experimental spectra were estimated by Fourier self-deconvolution (FSD) after base line correction, with a bandwidth parameter $W = 18\ \mathrm{cm}^{-1}$ and an enhancement parameter $K = 2.5$, as suggested by Kappers et al. [9] for Pt/KL catalysts.

The surface of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) with a VG Escalab 200R system using Mg Kα radiation (1253.6 eV). After reduction, the samples were introduced into the sample holder under isooctane which was removed during pumping in the preparation chamber of the XPS equipment. Since the Al 2p signal is coincident with that of Pt $4f_{3/2}$, the experimental spectra were deconvoluted and the resulting Pt $4f_{7/2}$ peak used to determine the electronic state of Pt.

2.3. Catalytic activity measurements

Dehydrocyclization of *n*-heptane was performed in a fixed bed tubular reactor, with 2 g of catalyst, at 723 K, 100 kPa, $\mathrm{WHSV} = 3.4\ \mathrm{h}^{-1}$ and $H_2/nC_7 = 7.3\ \mathrm{mol\ mol}^{-1}$. The catalysts were prereduced at 773 K under flow of hydrogen for 1 h and then, once the system was stabilized at 723 K, the *n*-heptane was fed and the first sample of the reactor effluent collected 15 min later in a condenser at 273 K. In order to check the stability of the catalysts, samples of the reactor effluent were periodically taken and analyzed by gas chromatography using a UCW98/Chromosorb W column. High purity hydrogen was successively passed through a Deoxo purifier and a 5A molecular sieve filter. Following a conventional methodology [10] it was verified that, under the experimental conditions used in this work, both external and internal diffusional limitations were absent.

Coke content of the catalysts after reaction was determined by temperature programmed oxidation (TPO) in a TG equipment heating 500 mg of sample from RT to 1073 K at $10\ \mathrm{K\ min}^{-1}$ in an O_2 flow of $100\ \mathrm{ml\ min}^{-1}$.

3. Results and discussion

3.1. Characterization of the catalysts

Table 1 summarizes Pt loading (Pt_T), dispersion (D), average particle size (d) and surface acidity (A) of the catalysts. Although the surface acidity of the samples is rather low, that of CE-3, prepared by ion exchange, is higher than that of the counterpart prepared by impregnation (CI-1), but the difference disappears when CE-3 is treated with KNO_3 (sample CE-3-n). On the other hand, the higher dispersion also corresponds to the catalysts prepared by ion exchange, which is an expected result because the exchangeable sites of the zeolite are homogeneously distributed in the framework. The average particle size values, similar to others reported for analogous catalysts [11] are larger than the dimensions of the cavities (0.48 nm × 1.24 nm × 1.07 nm) and windows (0.71 nm) of the zeolite. This result does not imply that platinum is only located on the external surface of the support but that, as it was evidenced by TEM–XEDS [12], there does exist a bimodal distribution of Pt particle size, i.e. Pt clusters inside the channels and Pt crystals at the external surface. From this, one can reasonably assume that the lower average crystal size the higher the fraction of Pt inside the zeolite.

Diffraction patterns of the catalysts display the main diffraction lines of the KL zeolite at $2\theta = 5.5, 11.77, 22.66, 28.00$ and $30.7°$ [13] showing that the crystallinity of the support is not modified during the preparation of the catalysts. Due to the high number of reflections present in the diffraction pattern of the zeolite, lines corresponding to Pt crystals were not perceptible.

Table 1
Characterization of the catalysts

Catalyst	CI-1	CI-2	CE-3	CE-3-n
Precursor	$Pt(NH_3)_4(OH)_2$	$Pt(NH_3)_4(NO_3)_2$	$Pt(NH_3)_4(OH)_2$	$Pt(NH_3)_4(OH)_2$
Pt_T (%)	0.98	0.97	0.99	0.97
D (%)	42	31	48	46
d (nm)	2.14	2.89	1.87	1.95
A (μeq g^{-1})	23	18	112	21

Pt_T, platinum loading; D, platinum dispersion; d, average metal particle size; A, surface acidity.

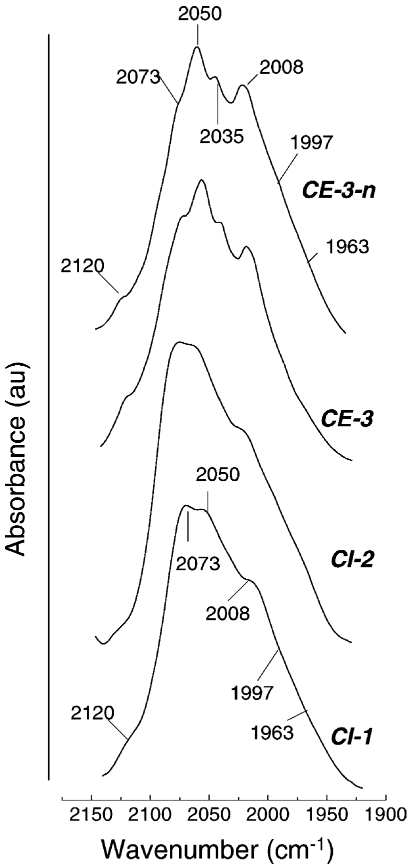

Fig. 1. FTIR spectra of CO adsorbed on the catalysts at room temperature and 4 kPa.

The CO–FTIR spectra of the samples exhibit a broad band in the range 2150–1920 cm^{-1} (Fig. 1) constituted by several simple overlapped bands. Using the Fourier self deconvolution method it was estimated the position of the band components at ca. 2120, 2073, 2050, 2035, 2008, 1997 and 1963 cm^{-1}, related to CO linearly bonded to different electronic Pt species [14]. Bands at wavenumbers lower than 1920 cm^{-1}, attributed to the bridging Pt carbonyls, are very weak.

The absorption band centered around 2073 cm^{-1} is usually ascribed to CO on large platinum particles, weakly interacted and located at the external surface of the zeolite [5,15]. Bands in the range 2050–1920 cm^{-1} (LFB) are assigned to electron rich platinum ($\mathrm{Pt}^{\delta-}$) within the channels, while that at 2120 cm^{-1} (HFB) is ascribed to vibrations of CO bonded to electron deficient platinum ($\mathrm{Pt}^{\delta+}$) at the outer surface [16,17].

Indirect confirmation of such a distribution of Pt species is derived from the XPS measurements. Since this technique analyzes the external surface of the pellets, it is expected that $\mathrm{Pt}^{\delta+}$ species are detected. XPS spectra in Fig. 2, corresponding to the CI-1 and CE-3 samples, exhibit the BE Pt $4f_{7/2}$ peak at 71.4 and 71.9 eV, respectively. These BE values, which are between the standards for Pt^0 (71.0 eV) and Pt^{2+} (72.5 eV), confirm the presence of electron deficient platinum species ($\mathrm{Pt}^{\delta+}$) and discard the location of $\mathrm{Pt}^{\delta-}$ at the outer surface. The higher BE value for CE-3 indicates, on the other hand, a higher electron

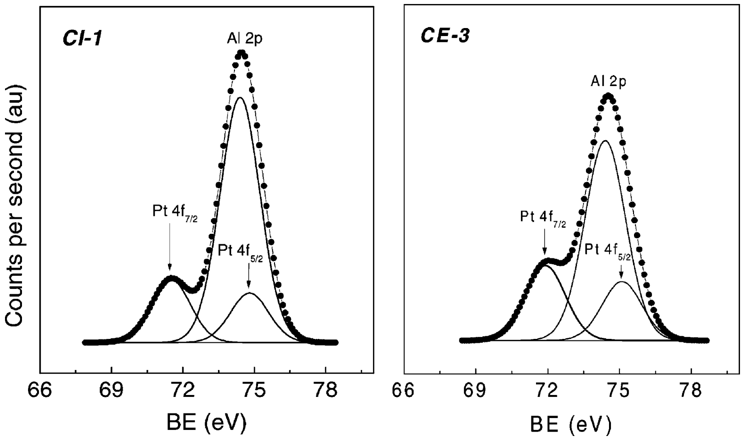

Fig. 2. Deconvoluted experimental XPS spectra of CI–1 and CE–3 catalysts with the component Pt 4f and Al 2p peaks.

deficiency in this sample as expected from the acidity values (Table 1), as it will be seen below.

From the examination of the IR spectra in Fig. 1, one can assert that the population and distribution of Pt species with different electron density depend on the identity of the Pt precursor and the method used to prepare the catalysts. So, comparing the spectrum of CI-2 with that of CI-1, it is observed a higher absorption intensity in the LFB zone ($Pt^{\delta-}$) while the intensity of the HFB ($Pt^{\delta+}$) is lower. This result indicates that the population of Pt clusters inside the channels in samples prepared by impregnation from $Pt(NH_3)_4(NO_3)_2$ is higher than that in the counterpart obtained from $Pt(NH_3)_4(OH)_2$. On the other hand, from the comparison of the CE-3 and CI-1 spectra it is deduced that the population of $Pt^{\delta-}$ particles within the channels in the ion exchanged sample is higher than in the impregnated one. The fact that the intensity of HFB in CE-3 is the highest evidences the important role played by the Brönsted acid sites formed during the reduction step of Pt^{2+} exchanged:

$$Pt^{2+}(ZO^-)_2 + H_2 \rightarrow 2ZO - H^+ + Pt^0 \qquad (1)$$

ZO^- being an ion exchange site of the zeolite.

Reaction (1) does not occur when the oxidized precursors of CI-1 and CI-2 are reduced because, in these samples, Pt upon calcination is present as PtO:

$$PtO(ZO - K) + H_2 \rightarrow (ZO - K)Pt^0 + H_2O \qquad (2)$$

Acid sites formed in reaction (1) interact with neighboring Pt^0 particles following the mechanism proposed by Sachtler and Stakheev [18] originating electron deficient Pt species. The fraction of such a species strongly decreases when CE-3 is ion exchanged with KNO_3 (sample CE-3-n). Likewise, an increase of the $Pt^{\delta-}$ signal is observed by FTIR. It is evident that ion exchange favors the location of Pt inside the channels and the posterior removal of protons formed increases the electron density of Pt particles.

3.2. Catalytic activity

The catalysts were evaluated in the dehydrocyclization of n-heptane to toluene at 723 K. In all the cases a decay of the initial dehydrocyclization activity as a function of the time on stream was observed until a pseudo steady state is reached after 2 h of reaction. Under these conditions the catalysts performance remains constant at least for 10 h. Results for the stabilized catalysts, summarized in Table 2, show that the major reaction product was toluene (Tol). The main by-products appear grouped as benzene (Bz), heptane isomers (i-C_7), hydrocracking products (C_2–C_6) and methane (C_1). Cycloalkanes and olefins were also observed in some experiments. Conversion (X) is defined as the percentage de n-heptane fed transformed into products; yield to a product i (Y_i), is the number of heptane molecules transformed into i percent molecules fed to the reactor. Selectivity toward toluene (S_{Tol}) is the number of molecules of heptane transformed into toluene per 100 molecules reacted. The turnover frequency of toluene (TOF_{Tol}) is the number of n-heptane transformed into toluene per exposed Pt atom and per second.

Table 2
Dehydrocyclization activity of the catalysts at $T = 723$ K; $H_2/nC_7 = 7.3$ mol mol^{-1}; WHSV $= 3.42$ h^{-1} and $P = 100$ kPa

Catalyst	CI-1	CI-2	CE-3	CE-3-n
X (%)	15.3	19.1	17.3	27.0
10^3 TOF_{Tol} (s^{-1})	28.2	45.4	21.6	51.5
Y_{Tol} (%)	6.4	9.1	5.6	12.8
Y_{bz} (%)	0.6	0.5	1.1	2.1
Y_{C1} (%)	0.5	0.1	2.2	2.8
$Y_{C2–C6}$ (%)	1.6	2.4	3.1	4.1
Y_{iC7} (%)	0.9	0.8	1.6	0.6
S_{Tol} (%)	42.0	47.0	32.0	48.0
Coke content (%)	0.6	0.5	0.9	0.3

X, conversion of n-heptane; Y, yield; S, selectivity.

The activity and selectivity values summarized in Table 2 are related to the physicochemical properties analyzed above and, indirectly, to the catalyst preparation conditions. So CI-2 (ex-nitrate) gives higher X, Y_{Tol}, TOF_{Tol} and S_{Tol} than CI-1 (ex-hydroxide) while CE-3, prepared by ion exchange, is a worse dehydrocyclization catalyst than those prepared by impregnation. In contrast, the sample CE-3-n appears to be the best aromatizing catalyst, evidencing the negative effect of the surface acidity on the dehydrocyclization reaction. Thus, it is clear that the higher the electron density of Pt within the zeolite the higher the yield to toluene. Coke content of the samples after reaction in turn correlates positively with the acidity values, as expected for a reaction occurring via carbenium ion.

4. Conclusions

The effect of the nature of the Pt precursor and the preparation method on both the physicochemical properties and dehydrocyclization activity of Pt/KL catalysts in the aromatization of *n*-heptane to toluene at 723 K have been analyzed.

The highest population of electron reach platinum species ($Pt^{\delta-}$) is found in CE-3-n, while the highest concentration of electron deficient platinum species ($Pt^{\delta+}$) appears in the CE-3 sample. The dehydrocyclization activity of the catalysts depends on the electronic state of Pt particles and their location in the zeolite which are, in turn, related to the nature of the metal precursor used and to the catalyst preparation method. The order of aromatizing activity, CE-3-n $>$ CI-2 $>$ CI-1 $>$ CE-3, roughly parallels the population of $Pt^{\delta-}$ inside the channels, the low aromatization selectivity of CE-3 being attributed to the Brönsted acid sites generated during the reduction of the Pt exchanged. These results support the conclusion that the higher the electron density of Pt particles inside the zeolite channels the higher the dehydrocyclization activity of Pt/KL catalysts.

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