Review

Pt-Pd/WO$_3$-ZrO$_2$ catalysts for isomerization-cracking of long paraffins

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ABSTRACT

The objective of this work was to optimize the acid function and metallic function of a Pt-Pd/WO$_3$-ZrO$_2$ catalyst for isomerization-cracking of long paraffins. The calcination temperature and the W content were the preparation variables varied and studied. The catalysts were tested in the reaction of *n*-decane isomerization-cracking. The focus of the optimization was put on the synthesis of a catalyst with a good isomerizing activity and a minimum activity for the formation of light gases. In this way an isomerizate of high octane number and high liquid yield would be obtained and used for blending into the gasoline pool. The catalysts were further characterized by temperature programmed desorption of probe molecules (TPD).

Varying both the W content and the calcination temperature enabled the regulation of the acid function properties. Thus both the activity and selectivity could be fine-tuned. The highest activity was obtained with the samples with a 15% of W and calcined at 700 °C. The samples calcined at 700 °C were also the most stable ones, i.e. the activity of the acid function was less affected by coking. All the prepared catalysts produced a high octane number gain that was between 75 and 95 points and low yields of light gases (<10%). Deactivation by carbonaceous deposits was attributed to coking on Lewis acid sites.

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Contents

1. Introduction

Successive crisis in the oil market have produced some decay of the global economic activity and have generated a movement to replace fossil fuel energy supplies. In spite of this the dependence of industrialized and underdeveloped countries on fossil fuels is still strong and the portion that these fuels occupy in the world energy supply will continue to be of 85–90%. With respect to the oil market the bigger changes in the near future are due to the following causes: (i) Non-availability of "attractive" crude oils, e.g. paraffinic and naphthenic crudes of low S, N and metal contents. This means refineries must process heavier crudes, with a higher content of polyaromatics, resins and asphalthenes. (ii) Increasingly stricter environmental laws, limiting the allowed contents of contaminants in fuels. Though product specifications vary from country to country the objectives for gasoline and diesel are the same: reducing sulfur and aromatics.

In the case of gasolines the loss of octane points produced by the gradual elimination of aromatics must be somehow compensated. Processes of isomerization and isomerization-cracking of normal

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paraffins are an alternative way of obtaining reformulated gasolines with high octane and low environmental impact. Nowadays hydroisomerization of paraffinic C_4–C_7 cuts is used in the refineries for the production of high octane gasolines [1–4] labelled as "ecologic". The isomerizate produced from light straight run naphtha is added to the gasoline pool. Other contributors to this pool are catalytic reforming naphtha and hydrotreated FCC naphtha. The high octane number supplied by branched paraffins compensates the octane loss produced by the elimination of environmental noxious aromatic compounds. Mild isomerization of heavier n-paraffins C_7–C_{15} is sometimes used for the production of diesel fuel with high cetane number and improved cold flow properties (viscosity, pour point, freezing point) [2,5,6]. Deeper branching of this cut could be used for producing isomerizate of high octane number for the gasoline pool provided that size adjustment is rebore or simultaneously performed. The unit operation doing so is the isomerization-cracking reactor.

Catalysts used in state-of-the-art isomerization-cracking reactors are bifunctional. They have a metal function providing de/hydrogenation and hydrogen activation properties that are usually supplied by Group VIII noble metals like Pt, Pd, Ni or Co [7,8]. The acid function is the support itself and some examples include acid zeolites, chlorided alumina and amorphous silica alumina. Noble metals have a positive effect over the activity and stability of the catalyst. However they have a low resistance to poisoning by sulfur and nitrogen compounds present in the processed cuts. Hydrogenation aromatics on noble metals is known to proceed with higher TOF and sulfur resistance when these are supported on acidic supports [9,10]. It has also been extensively reported that the addition of a second noble metal in close interaction with the first one greatly improves the resistance to poisons. The most remarkable case is that of the Pt-Pd synergy [11,12].

When the acid support is a zeolite two additional problems arise in the transformation of heavy paraffins: (i) there exists a restricted access to the active sites of the large molecules due to the small pore size of zeolites; (ii) the strong acidity of H-zeolites favors successive cracking reactions producing larger quantities of low value gaseous products.

The properties desired in isomerization-cracking catalysts for treating C_7–C_{15} depend largely on the nature of the desired end product. If the main purpose is to improve the cold flow properties of a diesel fuel a mild isomerization of the linear chains is needed in order to decrease the pour and cloud points without affecting the cetane number to a great extent. In this sense catalysts with adequate pore size, low acidity and Pt loaded, have displayed very good performance in hydroisomerizations of long-chain normal paraffins. In contrast when a stream of highly branched isoparaffins for the gasoline pool is needed the catalyst must have enhanced isomerization and little cracking activity in order to increase the liquid yield and reduce the amount of light gases. For this purpose the acid and metal functions must be appropriately balanced. Pt promoted tungsten-zirconia (Pt/WZ) has been successfully tested for this application. One of its drawbacks is its low resistance to both sulfur and nitrogen compounds.

In a previous work [13] we have studied the effect of the addition of palladium on the performance of the acid and metal functions of a Pt/WZ catalyst and on the product yield and distribution of the isomerization-cracking of long linear paraffins. The results obtained in the n-octane reaction revealed that the simultaneous addition of Pt and Pd to a WZ catalyst produces a decrease of the total acidity and an increase of the de/hydrogenating capacity as compared to the Pt/WZ or Pd/WZ monometallic catalysts. In this way Pd addition becomes a way of modulating the acid and metal functions and optimizing them for

mild isomerization-cracking with maximum liquid yield. In that report no further optimization of the acid function was done.

The objective of the current work was to optimize the acid function of a Pt/WO$_3$-ZrO$_2$ catalyst modifying both the W content and the calcination temperature in order to improve the selectivity to branched isoparaffins and the resistance to coke deactivation. Further Pd promotion was also tried in order to improve the sulfur resistance of the thus synthesized catalyst by promotion with Pd. n-Decane was used as a model compound to assess the catalyst in isomerization-cracking. Preparation and activation conditions were varied in order to find the best ones for getting a maximum C_{5+} liquid yield and a maximum RON value in the product isomerizate.

2. Experimental

2.1. Catalysts preparation

Zr(OH)$_4$ was obtained by hydrolysis of zirconium oxychloride (Strem Chem., 99.99%) in basic ammonia solution. The precipitate was washed and dried in a stove at 110 °C for 24 h. The sample was named ZH.

WO$_3$-ZrO$_2$ (WZ) was obtained by incipient wetness impregnation of ZH with a solution of ammonium metatungstate (Aldrich, >99.9%) previously stabilized at pH 6 for a week and of an adequate concentration in order to obtain two different W contents on the final catalyst (7.5 and 15%). This procedure is known to enrich the solution in medium size tungstate anions [14]. After the impregnation, the support was dried in a stove at 110 °C overnight. Finally it was calcined in air for 3 h at different temperatures (600, 700 and 800 °C).

The thus obtained WZ catalysts were impregnated with Pt and Pd using an incipient wetness technique. A mixture of aqueous solutions of Pt and Pd salts was used. Chloroplatinic acid (H$_2$Cl$_6$Pt·6H$_2$O, Strem 99.9%) was used as a Pt precursor and palladium chloride (Cl$_2$Pd, Strem, 99.9%) was used as Pd precursor. The concentrations of Pt and Pd in the impregnation solution were adjusted in order to get a 0.5% Pt and 0.27% Pd in the final catalyst. These weight percentages yield a Pt:Pd atom ratio of 1:1. Then the catalysts were dried at 120 °C and calcined in air (10 ml min^{-1}) for 3 h at 450 °C. Then they were ground and sieved to 35–80 meshes and they were used in these form for all characterization tests. Before the catalytic activity tests the catalysts were reduced in a hydrogen stream at 300 °C for 2 h.

2.2. Catalysts characterization

The chemical analysis of the Pt and Pd content of the solids was determined by atomic emission spectroscopy (ICP-AES) using an ARL model 3410 equipment. The solids were dissolved in a digestive pump with a mixture of 1 ml sulfuric acid, 3 ml hydrochloric acid and 1 ml nitric acid. The W content was determined by X-ray fluorescence.

X-ray diffraction spectra were measured in a Shimadzu XD-1 equipment with Cu Kα radiation filtered with Ni. The spectra were recorded in the 2θ range between 20° and 65° and with a scanning rate of 1.2° min^{-1}. The percentage of tetragonal phase of the samples was calculated using Eq. (1) [15]. The peaks located at $2\theta = 28°$ and 31° were attributed to the monoclinic phase of zirconia and those located at $2\theta = 30°$ to the tetragonal phase. The peaks located at $2\theta = 23$–25° were attributed to WO$_3$ crystals.

$$X_t (\%) = 100\alpha \frac{I_t}{(I_m + \alpha I_t)} \qquad (1)$$

X_t (%) = content of the tetragonal phase, $\alpha = 0.81$, I_t = integrated intensity corresponding to the (1 1 1) tetragonal peak, I_m = sum of the integrated intensities of the (1 1 1) and (1 1 −1) monoclinic peaks. The quantification of the amount of each crystalline phase and the amount of amorphous matter was made by Rietveld Quantitative Analysis (RQA). From these values the crystallinity percentage was calculated. Calibration constants were computed from reliable structural data.

The physical properties of the catalysts were determined from nitrogen physisorption data. Nitrogen adsorption was performed in a Micromeritics 2100 E equipment at the temperature of liquid nitrogen.

The reducibility of the samples was analyzed by means of temperature programmed reduction (TPR) in an Ohkura TP2002 apparatus equipped with a thermal conductivity detector. The samples were calcined in air for 1 h at 450 °C, cooled and stabilized in Ar at 25 °C and then heated to 900 °C at a rate of 10 °C min^{-1} in a stream of 4.8% H_2 in Ar.

The amount and strength of the acid sites were assessed by means of temperature programmed desorption of a basic probe molecule. Pyridine (Merck, >98%) was used to test both Brönsted and Lewis acid sites. Trimethyl pyridine (Merck, 99%) was used to probe the Brönsted acid sites and to calculate the Brönsted/Lewis ratio. The samples were first calcined for 1 h at 450 °C and then they were cooled in dry nitrogen to room temperature and immersed in a vial containing pyridine. The vial was closed and left for 6 h. Then the vial was opened and the samples were filtered and dried in still air at room temperature. The samples were then placed in a quartz microreactor and stabilized in N_2 for 1 h at 100 °C. Then they were heated from this temperature to 650 °C at 10 °C min^{-1}. The desorbed products were continuously analyzed in a flame ionization detector and the signal recorded in a computer connected on-line. The acid sites were classified as weak, mild or strong depending on the range of desorption of pyridine and trimethylpyridine. Sites desorbing between 150 and 300 °C were considered "weak" acid sites. Sites desorbing between 300 and 500 °C were considered "mild" and sites desorbing between 500 and 650 °C were considered "strong".

The amount and nature of the coke deposited on the catalysts at the end of the accelerated deactivation and regeneration tests was determined by means of temperature programmed oxidation. 0.04–0.06 g of the coked catalyst were loaded in a quart reactor and stabilized in N_2. Then the nitrogen stream was replaced by a mixture of 5% O_2 in N_2 (60 cm^3 min^{-1}) and the cell temperature was raised from 30 to 650 °C at a heating rate of 10 °C min^{-1}. Coke deposits were burned and the combustion gases converted to methane and quantitatively measured in a continuous way with a flame ionization detector. The total carbon concentration of the catalyst samples was obtained by integration of the TPO trace and by reference to TPO tests of samples with a known amount of carbon.

2.3. Catalytic tests

Before measuring the catalytic activity all samples were pre-treated in situ in the reactors. First they were calcined in air (1 h, 450 °C) and then in hydrogen (1 h, 300 °C). At the pressure, temperature and flow rate conditions chosen for each reaction, neither internal nor external mass transfer limitations in the catalyst particles were found, as confirmed by the calculation of the Weisz-Prater modulus ($\Phi < 0.01$) and the Damköhler number ($Da \approx 0$).

2.3.1. Hydroisomerization-cracking of n-decane

This reactor was performed in a fixed bed tubular reactor with 0.25 g of catalyst, at 0.1 MPa, $T = 300$ °C, WHSV = 1 h^{-1} and molar ratio $H_2/nC_{10} = 6$. The products were analyzed on-line by chromatography using a 100 m capillary column coated with squalane. From these chromatographic data conversion and yields to different products were calculated.

2.3.2. Octane gain

The calculation of the Research Octane Number (RON) of the product mixture was done by applying a simple non-linear method that uses compositional GC data. The method is described in ref. [16]. The RON gain (ΔRON) was defined as the difference between the RON of the product mixture and the RON of *n*-decane. The percentage of light gases was calculated as the mass fraction of C_1–C_4 in the product mixture.

3. Results and discussion

Table 1 contains results related to the composition and textural and crystal properties of the synthesized catalysts. Chemical analysis confirmed that the W weight contents were 7.5 and 15% for all catalysts within a 5% error margin that was considered negligible.

With respect to the surface area it can be seen that the final available area depends mainly on the temperature of calcination and the W content. As previously reported [17,18] the addition of different oxoanions to Zr(OH)$_4$ (ZH) and its calcination at high temperatures produce great modifications on its properties. Calcination produces three consecutive processes, loss of loosely bound water, oxolation of adjacent hydroxyl bridges with

Table 1
Textural and compositional properties of the samples

Sample	Calculated temperature (°C)	W (atoms nm^{-2})	W (wt%)	Pore volume (cm^3 g^{-1})	Sg (m^2 g^{-1})	Crystal phase		Crystallinity (%)
						ZrO$_2$	WO$_3$	
ZH	100	–	–	–	262	A	–	–
Z	620	–	–	–	37	18% T, 82% M	–	89
WZ	500	4.5	15	–	110	A	–	–
WZ	600	6.2	15	–	80	T	–	81
WZ	700	7.8	15	–	63	T	–	88
WZ	800	12.6	15	–	39	T	M	91
PtPdWZ	600	4.6	7.5	0.133	53	T	–	–
PtPdWZ	700	5.6	7.5	0.109	44	T	–	–
PtPdWZ	800	6.6	7.5	0.108	37	T	–	–
PtPdWZ	600	6.2	15	0.123	79	T	–	–
PtPdWZ	700	9.1	15	0.116	54	T	–	–
PtPdWZ	800	11.1	15	0.115	44	T	M	–

T: tetragonal, M: monoclinic, A: amorphous.

structural water loss and nucleation and growth of zirconium oxide crystals. The oxide first stabilizes into its tetragonal (T) phase in spite of the monoclinic (M) phase being the thermodynamically favoured one. At small crystal sizes the higher surface energy of the monoclinic phase precludes the crystal growth of zirconia into this habitat and favours the stabilization of the tetragonal phase in a metastable condition. Interaction of the W species with the zirconia surface also stabilizes the T phase and slows down the crystallization and sintering processes. For this reason W promoted catalysts are less crystalline and have a higher specific surface area than unpromoted zirconia for the same temperature of calcination. The surface area of ZrO_2 after calcination at 800 °C is 8 $m^2\,g^{-1}$. The stabilizing effect depends on the surface concentration of W and is stronger for the samples with 15% W that have the highest specific surface area values. For the same calcination temperature the specific surface area increases with the amount of W until a limit value is obtained that coincides with the point of formation of a stable monolayer of W [18].

The addition of W to ZH and its subsequent calcination yielded samples with different crystal phases depending on the temperature of calcination (T_c). Higher T_c values produced samples with higher crystallinity. XRD peaks related to the tetragonal phase of zirconia were mainly detected. In PtPd/15WZ[800] a segregated phase of monoclinic WO_3 crystallites appeared in the XRD spectrum. The appearing of WO_3 as a separated phase occurred for W surface concentrations between 7.8 and 12.6 W atoms nm^{-2}, in coincidence with the reports of Barton et al. [18] that say that the surface saturation value is 9.0 atoms W atoms nm^{-2}.

As it was pointed out earlier an important issue to take into consideration when reacting heavy cuts is the porosity of the catalyst and particularly its pore size distribution. The results of the measurements are plotted in Figs. 1 and 2. In both cases mesoporous supports were obtained with pore diameters between 30 and 150 Å. These samples should pose lower mass transfer limitations to bulky molecules than zeolitic catalysts due to the relatively larger diameter of their pores. This is an important advantage over these catalysts, that are commonly used in hydroisomerization processes, e.g. for the isodewaxing of heavy lubes.

In both cases after increasing the calcination temperature a decrease of the amount of pores smaller than 100 Å was produced with a parallel increase of those pores between 100 and 300 Å. This shift in the distribution correlates with the decrease in specific surface and total pore volume as seen in Table 1.

Another crucial property when processing heavy feedstocks is the total acidity and the distribution of acid strength. An
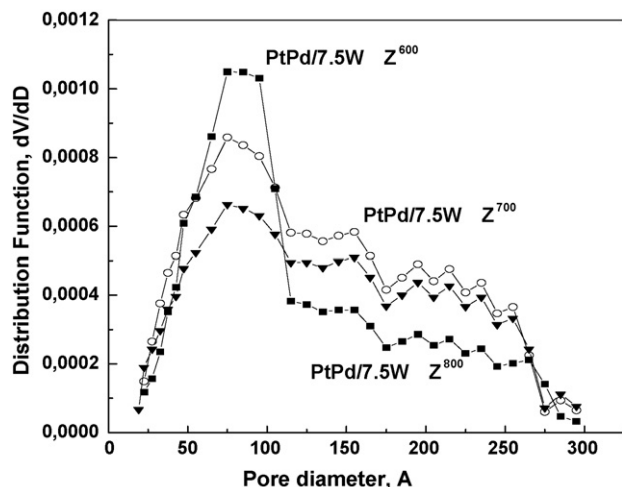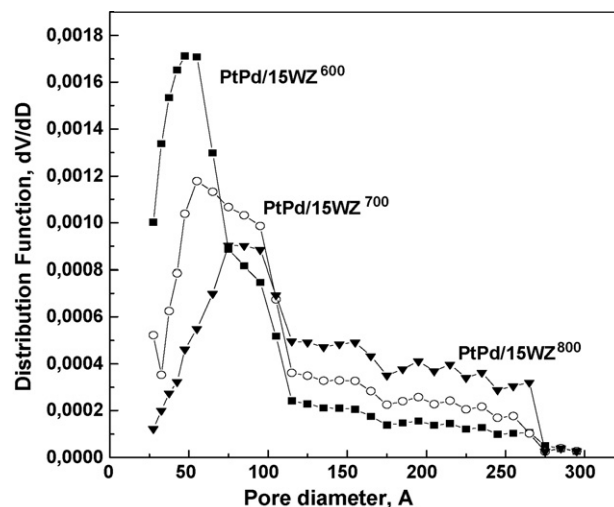

Fig. 2. Pore size distribution of PtPd/15WZ calcined at different temperatures.

appropriate acid amount and an appropriate distribution are required in order to minimize cracking and formation of light gases while producing a good yield of branched isomers. The amount and acid strength are both largely dictated by the W content and the calcination temperature. Zhang et al. [19] studied the hydroisomerization of *n*-hexadecane over Pt/WZ catalysts of varying W content and they found that the acidity increased at higher W loadings and that the selectivity to different isomers depended on the relative concentration of weak, mild and strong acid sites. In other works [13,17] it has been reported that the addition of Pt to WZ calcined at 700 °C produces an increase of the total acidity while keeping the relative distribution of acid strength unaltered. Our previous work with the PtPd/WZ system [13] indicates that the simultaneous addition of Pt and Pd reduces the total concentration of acid sites of the catalyst and favours the increase of the fraction of mild acid sites.

Total acidity and acid strength distribution (Total/Brönsted acidity ratio) results as measured by temperature programmed desorption of pyridine and trimethyl pyridine, expressed as surface concentration of acid sites are included in Table 2. In contrast to previous results the total acidity decreases slowly at higher W contents, for a same calcination temperature. However for both W contents the maximum acidity is obtained after calcination at 700 °C. Lower total acidity values are obtained at the other calcination temperatures. Another common feature is that sites of mild acid strength are more abundant than weak and strong acid sites. This relative dominance of mild acid sites occurs also for samples calcined at 700 °C. They comprise 65–70% of the total population. At 600 °C they are 54–58% and at 800 °C they are 45–48%. The surface concentration of strong acid sites increased with the calcination temperature for both W contents studied and was maximum for the catalysts calcined at 800 °C. In this case the relative proportion of strong acid sites was maximum, 36–39%.

The data of the TPD of pyridine and TMP were used to determine the relative amount of Brönsted and Lewis sites. For both series of catalysts the B/L ratio depended on the amount of W and the calcination temperature. Therefore for the same W content calcination at 700 °C produces a maximum in the B/L ratio. On the other side the Brönsted/Lewis ratio of WZ increased with the W content indicating that one effect of W is to enhance the stability of protonic acid sites at all calcination temperatures. However the B/L ratio decreased at high temperatures due to dehydration and transformation of Brönsted into Lewis acid centers. In all cases the weak acid sites are mainly Brönsted sites while the stronger ones

Fig. 1. Pore size distribution of PtPd/7.5WZ calcined at different temperatures.

Table 2
Total acidity and acid strength distribution (total/Brönsted acidity ratio)

Catalyst	Acidity (sites nm^{-2})							B/L ratio
	Total (L + B)	Weak 150–300 °C		Mild 300–500 °C		Strong 500–650 °C		
		L + B	B	L + B	B	L + B	B	
PtPd/7.5WZ^{600}	0.91	0.16	0.13	0.65	0.09	0.10	0.00	0.19
PtPd/7.5WZ^{700}	1.23	0.17	0.12	0.86	0.24	0.20	0.01	0.43
PtPd/7.5WZ^{800}	1.13	0.17	0.14	0.55	0.10	0.41	0.01	0.31
PtPd/15WZ^{600}	0.57	0.09	0.07	0.31	0.06	0.17	0.00	0.25
PtPd/15WZ^{700}	0.89	0.11	0.08	0.58	0.16	0.20	0.00	0.66
PtPd/15WZ^{800}	0.84	0.12	0.10	0.39	0.06	0.33	0.01	0.30

L: Lewis acid sites, B: Brönsted acid sites.

are mainly of the Lewis type. The strongest acid sites are exclusively Lewis.

It can be concluded that the W content and the calcination temperature of the base catalyst not only affects the total acidity and the acid strength distribution but also the relative amount of Brönsted and Lewis sites. Regardless of the W content, calcination at 700 °C generates an adequate acid strength distribution with mostly mild Brönsted sites of high isomerizing and low cracking activities. It is known that Lewis sites preferentially catalyze cracking reactions associated with the formation of coke [20].

The TPR results of the Pt-Pd catalysts calcined at different temperatures are included in Fig. 3. The trace of the zirconia support without Pt, Pd or W had no detectable peaks. With respect to the PtPd/WZ a zone of early reduction is found at 50–200 °C. Depending on the calcination temperature one or two peaks are found in this zone. The low temperature peak can be readily assigned to the reduction of Pd oxide species while the higher temperature peak can be attributed to the reduction of Pt oxide species [21].

With respect to the reduction of the tungsten species the TPR trace developed many peaks corresponding to the reduction of tungsten oxides of varying oxidation state. The reduction profiles of these tungsten oxides species are wide and three different reduction peaks can be identified. At 300–500 °C WO$_3$ is converted into substoichiometric WO$_{2.9}$. At 550–700 °C substoichiometric WO$_{2.9}$ converts into stable WO$_2$. At 750–850 °C the latter is finally reduced to metallic W. Peaks at higher temperature and in the 900–950 °C would correspond to the reduction of WO$_x$ species in
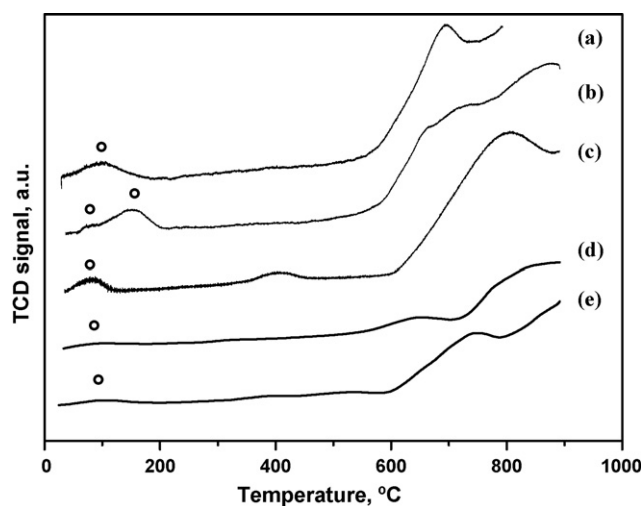
strong interaction with the support. This interaction is due to stable and refractory Zr–O–W bonds. The WZ sample calcined at 800 °C had four peaks that could possibly match the previously described reduction zones. The first peak at 380 °C should be related to the reduction of bulk WO$_3$ into substoichiometric trioxide. In fact some crystallites of WO$_3$ can be found as revealed by the XRD spectrum of this sample. The second peak with a maximum at 700 °C should be related to the WO$_{2.9} \rightarrow$ WO$_2$ transition and the third peak centered at 770 °C should correspond to the WO$_2 \rightarrow$ W transition [18]. Regarding the size of the second peak this has been reported to be sensitive to the size of the WO$_x$ clusters. The bigger the size of the cluster the higher the proportion of W–O–W bonds (and the lower proportion of Zr–O–W ones) and the lower the temperature that is needed for their reduction. Barton et al. [18] have found that the isomerization activity for n-paraffin isomerization seems to correlate with the concentration of the WO$_x$ clusters of medium size. They have suggested that this cluster size allows the reduction of WO$_{2.9}$ into WO$_2$. Vera et al. [22,23] have suggested that for the isomerization of n-paraffins over oxoanion promoted zirconia catalysts the delocalization of charge is crucial for the stabilization of surface carbocations. According to the early reports of Hattori and coworkers [24] on the dynamic formation of Brönsted acid sites in a reducing hydrogen atmosphere, surface reducible species are needed for the generation of protonic acid sites. The fourth peak of the TPR trace of the WZ catalyst (at about 900 °C) has the biggest area and would be related to the reduction of WO$_x$ strongly bonded to the support. The sample calcined at 700 °C had similar peaks and they should therefore correspond to both WO$_x$ surface species and segregated WO$_3$ crystals. The sample calcined at 600 °C had only a reduction peak related to the high temperature reduction of surface WO$_x$ species interacting with the support.

Fig. 4 contains two plots of the total conversion of n-decane as a function of time-on-stream (TOS) for all tested samples. The two plots make a comparison between the results corresponding to 7.5% W catalyst and those corresponding to the 15% W catalyst. All the catalysts had high levels of initial conversion that were above 70%. Particularly the samples calcined at 700–800 °C had total conversion values higher than 85%. Among the Pt-Pd containing samples the PtPd/7.5WZ catalyst calcined at 800 °C had the maximum initial activity with a conversion of about 92%. PtPd/15WZ calcined at the same temperature showed a somewhat lower value (83%). A calcination temperatures of 600 °C produces less active catalysts. In all catalysts the values of total conversion increase with the calcination temperature except for the sample with 15% W calcined at 800 °C. Its conversion is lower than that displayed by the same catalyst calcined at 700 °C. The maximum conversion value is obtained with the Pt/15WZ^{700} catalyst (98%).

All catalysts showed similar trends with increasing time-on-stream (TOS). Deactivation was a consequence of the formation of surface coke being faster during the first 20 min. The deactivation
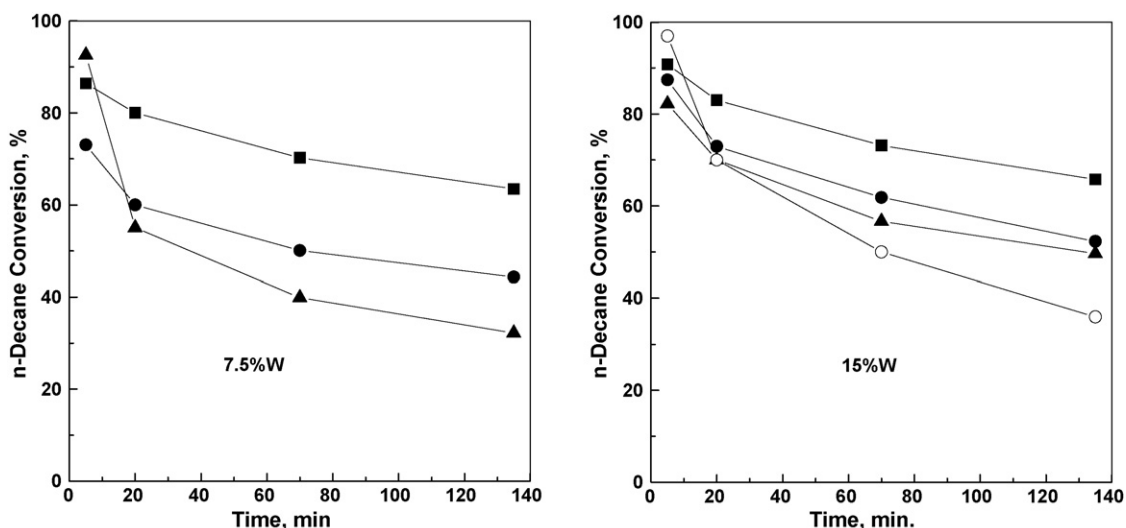

Fig. 3. Traces of temperature programmed reduction of the catalyst samples. (a) PtPd/15WZ^{600}; (b) PtPd/15WZ^{700}; (c) PtPd/15WZ^{800}; (d) PtPd/7.5WZ^{600}; (e) PtPd/7.5WZ^{700}. (○) Noble metal low temperature reduction peaks.

Fig. 4. Conversion of *n*-decane as a function of time-on-stream. PtPd/WZ catalysts calcined at 600 °C (■), 700 °C (●) and 800 °C (▲). Pt/WZ catalyst calcined at 700 °C (○).

rate was higher for the samples calcined at 600 and 800 °C irrespective of the W content. At 135 min the samples calcined at 700 °C lost 27% of their original activity while the other samples lost 40–65%. Pt/15WZ[700] lost 63% of its original activity. At this reaction time none of the samples could reach a stationary state with respect to activity or selectivity. Moreover they continued to deactivate.

The catalytic activity of the samples depended both on the W content and the calcination temperature. We could say that the promotion with Pt or Pd notably improved the stability of the catalysts. Calcination at 700 °C of the 7.5–15% W content catalysts provides the best catalysts from the point of view of the high activity in the *n*-decane reaction and also considering the stability to deactivation by coking.

Temperature programmed oxidation of the coke deposits was performed on samples after 135 min of time-on-stream (Table 3). Integration of the area under the TPO trace yields the total amount of deposited carbon. The amount of this on the catalysts was small (<2%), indicating that only a small fraction of the surface sites was affected by it. These carbon deposits would be too small to justify the decrease of the conversion in the tested samples. The catalysts with 7.5% W had bigger carbon deposits than the catalysts with 15% W. In both series the samples calcined at 700 °C had lower carbon deposits. Besides and as it was previously indicated both samples had similar patterns of conversion as a function of time. However after 135 min time-on-stream the sample with 7.5% W has 1.36% of carbon while the sample with 15% W only 0.5%.

The TPO traces (Fig. 5) showed in all cases a big peak located at 350–500 °C that would correspond to the combustion of highly polymerized, hydrogen-deficient coke located on the acid sites of the support. No peaks at 200–350 °C were seen that could be attributed to the combustion of poorly polymerized coke,

hydrogen-rich, typically located on the metal particles or their surroundings [25,26].

One possible explanation to the coking behavior is that this is influenced by the mass transfer limitations appearing after the blocking of the catalyst pores. However this is not possible due to the small volume of carbon produced and the relatively big diameter of the catalyst pores. Another one more likely is that both the catalytic activity and stability are related to the relative concentration of Lewis and Brönsted acid sites.

Fig. 6 shows a plot of the coke content of the catalysts as a function of the number of surface Lewis acid sites. There is a good linear correlation between the two variables indicating that coke is preferentially formed on Lewis acid sites. Roussel et al. [27] postulated that *n*-decane transforms on sulfided NiW/silica-alumina catalyst through two possible reactions: bifunctional hydrocracking and "direct cracking". The activity loss may be due to the gradual coverage of Lewis sites with coke produced during the direct cracking of C_{10}.

Table 4 shows the values of total conversion, selectivity to normal paraffins and branched isoparaffins, RON gain (ΔRON) and the percentage of light gases (C_1–C_4 fraction) for different catalysts

Table 3
Coke deposition on PtPd/WZ catalysts after 135 min of time-on-stream

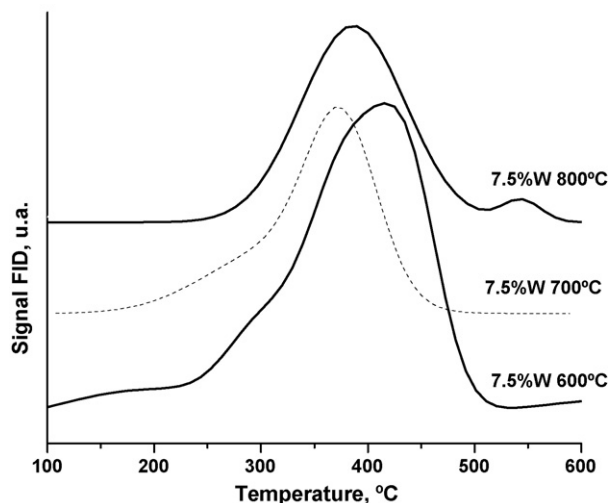| Catalysts	Carbon (wt%)
PtPd/7.5WZ[600]	1.54
PtPd/7.5WZ[700]	1.38
PtPd/7.5WZ[800]	1.61
PtPd/15WZ[600]	1.03
PtPd/15WZ[700]	0.50
PtPd/15WZ[800]	1.20

Fig. 5. TPO traces of the catalysts with 7.5% W calcined at different temperatures. Catalysts coked in the reaction of hydrocracking of *n*-decane.
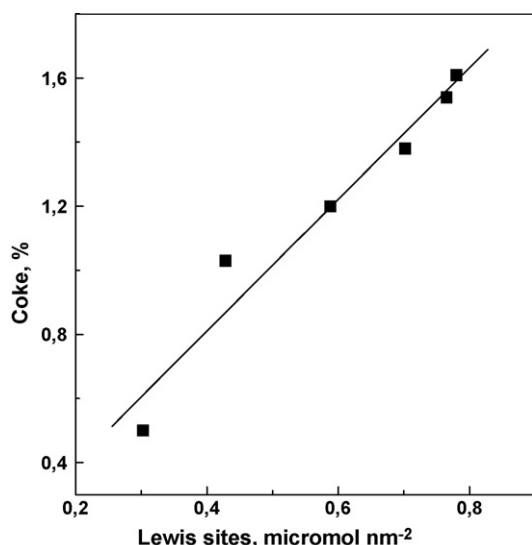
Fig. 6. Correlation between the amount of Lewis acidity and the amount of carbon deposits after the run.

at 5 min time-on-stream (results corresponding to the fresh, coke-free catalysts). It can be observed that: (i) Most products are normal paraffins and isoparaffins. (ii) Cyclization reactions occur with lower than 2% yields. (iii) Iso/normal paraffins ratio is greater than one in all series but it is maximum for the catalysts calcined at 600 °C. (iv) C_1, C_2, C_7, C_8, C_9 are negligible among normal paraffins. (v) i-C_{4-6} dominate the isoparaffins distribution while i-C_7 and i-C_9 are negligible.

The greater concentration of isoparaffins is expected from thermodynamics. As a first approximation the free energy of the alkane isomerization reactions is almost null and therefore the concentration of each isomer is roughly inversely proportional to the total number of isomers. There are 75 possible carbon isomorphic compounds containing 10 carbon atoms and therefore at thermodynamic equilibrium the normal/iso ratio can be as low as 1/74. This ratio is never attained in practice because many of the isomers are kinetically hindered, i.e. the chemical route to its formation has too many steps or has some step of a high activation energy.

Isomerization is always accompanied by some extent of cracking. The well-accepted classical mechanism of isomerization and cracking of a linear paraffin necessarily begins with a first step of adsorption of a carbenium ion. This is likely firstly isomerized in the adsorbed state by any of the accepted mechanisms such as methyl shift or formation of protonated cyclopropanes. Cracking is a consecutive reaction which is favored for multibranched paraffins. The branched isomer can be cracked on the same site or can readsorb on another site and be cracked there. Cracking can only proceed on acid sites with a strong acidity. In an "ideal" isomerization-cracking scheme molecules resulting from primary cracking are desorbed and are not subjected to secondary cracking and in this way the formation of light gaseous products is minimal.

As it can be seen in Table 4 in all cases i-C_4, i-C_5 and i-C_6 are the most abundant isomers confirming that cracking in the middle position of paraffin molecule is favored. The absence of C_1 indicates that hydrogenolysis is completely suppressed, a fact related to the inhibition of the metal function of noble metals on oxoanion promoted zirconia [27,28]. C_2 is also absent and therefore cracking in the beta position is also disfavored. The inhibition of both alpha and beta cracking prevents much of the secondary cracking for such a middle-length molecule as n-decane.

Monobranched isoparaffins are the dominating species. This is partly due to the fact that multibranched ones are more easily cracked and on some strong acid sites multibranching might be followed by cracking. It might also be the consequence of a relatively short residence time as it can be inferred from the moderate total conversion. At very low conversion monobranched isomers should be formed exclusively. With increasing overall conversion, the content of dibranched isomers increases monotonically at the expense of the monobranched isomers, then multibranched isomers are formed very rapidly and undergo cracking yielding mainly branched products.

The obtained values of RON gain were between 84 and 96. These values are quite high. Pt/15WZ^{700} yields the greatest RON gain of 96 points. In the case of the double promoted Pt-Pd samples the best catalyst is PtPd/7.5WZ^{800} (94 points of RON gain).

The branched pentane isomers, 3,3-dimethyl-propane and 2-methyl-butane, have a blending RON of 99-100 while branched hexane isomers, 2-methyl-pentane, 3-methyl-pentane, 2,2-dimethyl-butane and 2,3-dimethyl-butane, have blending RON values of 83–96. Heptane branched isomers have an average of 70

Table 4
Total conversion (X_T), selectivity to normal paraffins (S_{nP}), selectivity to isoparaffins (S_{iP}), yield of light gases, octane gain of the liquid fraction (ΔRON) and yields to different compounds at 5 min time-on.-stream

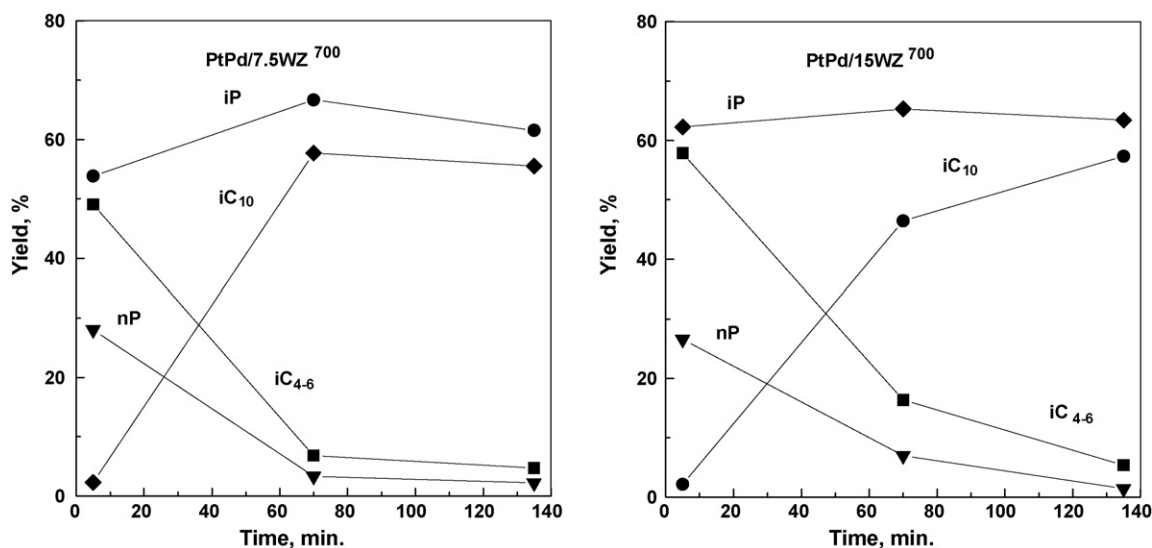|	7.5%W			15%W			PtWZ
	600 °C	700 °C	800 °C	600 °C	700 °C	800 °C	
X_T (%)	72.68	86.16	92.25	87.09	90.28	81.95	98.00
S_{nP} (%)	25.69	36.41	33.80	27.72	29.43	28.35	44.52
S_{iP} (%)	71.98	61.91	65.40	70.24	68.94	70.50	55.28
C_1–C_4 (%)	29.80	24.79	34.30	20.48	24.78	26.62	36.66
ΔRON	84.36	91.00	94.36	87.84	91.53	86.82	96.05
nC_3 (%)	8.65	5.45	7.48	3.54	4.38	5.28	0.22
nC_4 (%)	7.61	7.40	8.51	5.19	5.67	7.34	28.36
nC_5 (%)	5.44	12.82	9.59	8.74	9.67	7.88	10.31
nC_6 (%)	3.99	9.81	7.40	7.84	8.26	6.39	5.63
nC_7 (%)	0.00	0.94	0.00	1.03	0.88	1.46	0.00
nC_8 (%)	0.00	0.00	0.83	0.66	0.00	0.00	0.00
nC_9 (%)	0.00	0.00	0.00	0.72	0.56	0.00	0.00
iC_4 (%)	24.75	15.94	21.19	14.78	17.39	19.87	8.12
iC_5 (%)	26.78	20.01	23.91	20.51	23.74	24.77	22.67
iC_6 (%)	20.45	20.96	20.31	21.46	22.92	21.93	22.23
iC_7 (%)	0.00	2.66	0.00	3.65	2.54	2.12	0.56
iC_{8-10} (%)	0.00	2.35	0.00	9.83	2.34	1.81	1.62
Aromatics (%)	0.00	0.65	0.00	1.06	0.75	0.50	0.00

Fig. 7. Values of yield to different products. Catalysts calcined at 700 °C.

RON points. From the point of view of the isomerizate cracking in middle positions favors the final RON value. Branched isomers of octane (not taking trimethylpentane into account), nonane and decane supply less than 30 RON points to the mixture. Summarizing, the greater the content of pentane branched isomers in the mixture the greater the RON gain.

A minimum production of light gases and a maximum liquid yield are fundamental for sustaining the economy of any refining unit producing liquid fuels. The liquid yield values for almost all the catalysts were 70–80% and were higher than others reported for commercial zeolitic catalysts for a similar conversion [29]. Isobutane concentration was high among the light gases. In spite of being a valuable compound maximization of the isobutane yield is not an issue in this work because it would lower the liquid C_{5+} yield. It is also important to minimize the C_4 yield in order to decrease butane and isobutane dissolved in the gasoline that would increase the volatility of the fuel and would exceed the Reid Vapor Pressure limit established by current environmental standards.

Comparatively the samples with 15% W are those producing the minimum amount of gases. In the series, the sample calcined at 600 °C shows the lowest light gases yield, 20.4%. This is 4–14 less points than the rest of the catalysts containing both Pt and Pd. Pt/15WZ-700 produces 36.6% light gases.

Fig. 7 shows the yields to several products as a function of time-on-stream for two Pt-Pd different catalysts, 7.5 and 15% W, calcined at 700 °C. The rest of the catalysts had similar yields-time patterns. A few things are relevant to these patterns. (i) The yield to isoparaffins is almost constant despite the deactivation during the reaction. It could be said that sites responsible for isomerization are scarcely affected by growing carbon deposits. (ii) The yield to i-C_{4-6} and total n-paraffins decreases with TOS while the yield to i-C_{10} grows in the same extent. If as it is assumed both isomerization and cracking sites are different the results would indicate that only the cracking sites are deactivated. These cracking sites would mostly be Lewis acid ones. At 135 min TOS practically all the cracking activity has been lost.

The results indicate simultaneous addition of Pd and Pt notably improved the liquid yield without affecting the RON gain of the reaction. Adjusting the calcination temperature and the W load enables to optimize the stability, the liquid yield and the RON gain.

4. Conclusions

W content and calcination temperature greatly affect the physicochemical and catalytic properties of tungsten-zirconia catalysts double promoted with Pt and Pd. The adequate manipulation of these variables enables an adequate fine tuning of the acid amount and strength distribution. These translates into catalysts for isomerization-cracking of long paraffins with enhanced liquid yield, and RON gain.

Best values in isomerization-cracking are obtained with samples with a 15% W calcined at 700 °C. Samples calcined at 700 °C also display the lowest deactivation rates.

All catalysts produced RON gain values of 75–95 points. They also had good values of formation of light gases. Catalysts calcined at 700 °C showed the highest yields to isobutane but had the lowest values of liquid yield.

The coking of the catalysts seems to proceed to a great extent on Lewis acid sites and a good correlation between coke content and concentration of surface Lewis acid sites was found.

Acknowledgements

References

[1] S.J. Miller, Stud. Surf. Sci. Catal. 84 (1994) 2319.
[2] P. Mériaudeau, V.A. Tuan, V.T. Nghiem, S.Y. Lai, L.N. Hung, C. Naccache, J. Catal. 169 (1997) 5.
[3] N.A. Cusher, P. Greenouch, J.R.K. Rolfe, J.A. Weiszmam, Handbook of Petroleum Refining Process, McGraw-Hill, New York, 1986.
[4] A. Corma, Catal. Lett. 22 (1993) 33.
[5] E. Blomsma, J.A. Martens, P.A. Jacobs, J. Catal. 165 (1997) 241.
[6] J.A. Martens, G. Vanbutsele, P.A. Jacobs, J. Denayer, R. Ocakoglu, G. Baron, J.A. Muñoz, J. Thybaut, G.B. Marin, Catal. Today 65 (2001) 111.
[7] R.C. Dougherty, D.N. Mazzone, European Patent EP 782,608 (2007).
[8] I.A. Cody, D.H. Dumfried, A.H. Neal, K.L. Riley, US Patent 5,182,248 (1993).
[9] B. Pawelec, R. Mariscal, R.M. Navarro, S. van Bokhorst, S. Rojas, J.L.G. Fierro, Appl. Catal. A Gen. 225 (2002) 223.
[10] A.P. Jansen, R.A. van Santen, J. Phys. Chem. 97 (1990) 6764.
[11] M.A. Vannice, R. Prins, Catal. Today 123 (2007) 198.
[12] K. Thomas, C. Binet, T. Chevreau, D. Cornet, J.-P. Gilson, J. Catal. 212 (2002) 63.

[13] J.C. Yori, R.J. Gastaldo, V.M. Benítez, C.L. Pieck, C.R. Vera, J.M. Grau, New formulations of oxoanion promoted zirconia catalysts for the upgrade of heavy paraffinic cuts, Catal. Today 133-135 (2008) 339–343.

[14] J.C. Yori, J.M. Parera, Catal Lett. 65 (2000) 205.

[15] T.J. Itoh, Mater. Sci. Lett. 5 (1986) 107.

[16] N. Nikolaou, C.E. Papadopoulos, I.A. Gaglias, K.G. Pitarakis, Fuel 83 (2004) 517.

[17] V.M. Benítez, J.C. Yori, J.M. Grau, C.L. Pieck, C.R. Vera, Energy Fuels 20 (2006) 422.

[18] D.G. Barton, S.L. Soled, G.D. Meitzner, G.A. Fuentes, E. Iglesia, J. Catal. 181 (1999) 57.

[19] S. Zhang, Y. Zhang, J.W. Tierney, I. Wender, Appl. Catal. A 193 (2000) 155.

[20] K. Mizuno, M. Ikeda, T. Imokawa, J. Take, Y. Yoneda, Bull. Chem. Soc. Jpn. 49 (1976) 1788.

[21] B.L. Barrio, P.L. Arias, J.R. Cambra, M.B. Güemes, B. Pawelec, J.L. García Fierro, Fuel 82 (2003) 501.

[22] C.R. Vera, C.L. Pieck, K. Shimizu, J.M. Parera, Appl. Catal. A 230 (2002) 137.

[23] C.R. Vera, J.C. Yori, J.M. Parera, Appl. Catal. A 167 (1998) 75.

[24] K. Ebitani, J. Tsuji, H. Hattori, H. Kita, J. Catal. 135 (1992) 609.

[25] J.M. Parera, N.S. Figoli, E.M. Traffano, J. Beltramini, E.E. Martinelli, Appl. Catal. 5 (1983) 33.

[26] J. Barbier, P. Marecot, N. Martín, L.E. Lassa, R. Maurel, Stud. Surf. Sci. Catal. 6 (1980) 53.

[27] M. Roussel, S. Norsic, J.-L. Lemberton, M. Guisnet, T. Cseri, E.E. Benazzi, Appl. Catal. A: Gen. 279 (2005) 53.

[28] J.M. Grau, J.C. Yori, C.R. Vera, F.C. Lovey, A.M. Condó, J.M. Parera, Appl. Catal. A 265 (2004) 141.

[29] C.R. Vera, J.C. Yori, C.L. Pieck, S. Irusta, J.M. Parera, Appl. Catal. A 240 (2003) 161.