

Hydroisomerization–cracking of *n*-octane on Pt/WO₄²⁻–ZrO₂ and Pt/SO₄²⁻–ZrO₂ Effect of Pt load on catalyst performance

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Abstract

The hydroconversion (isomerization–cracking) of *n*-octane was studied at 300°C, 1.5 MPa, WHSV = 4 and H₂/*n*C₈ = 6 using oxoanion promoted zirconia with different Pt concentrations (0.1, 0.5 and 1%) as catalysts. Tungstate was added to zirconia by impregnation with ammonium *meta*-tungstate or tungstic acid solutions and calcined at 800°C. Sulfate was added by impregnation with 2N H₂SO₄ and calcined at 620°C. Isooctanes are intermediate products that are cracked to C₃–C₅ alkanes with predominance of isoalkanes. Sulfate zirconia is the most active and selective catalyst to cracking products. The addition of 0.1% of Pt produces an increase in activity and stability, respect of the support without metal. However, the increase in Pt content (0.5 and 1.0%) produces a decrease in *n*C₈ conversion and in cracking products. The metallic properties of Pt are decreased by its strong interaction with the support, mainly with sulfate zirconia; at the same time, Pt decreases the acid cracking activity of the support. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The increasing demand of reformulated gasoline has led to the research into new technological routes and new catalysts for the production of high octane compounds less dangerous to the environment. For this objective, light isoalkanes (C₄–C₆) are very important materials. Isobutane (*i*C₄) is used as raw material for alkylates and MTBE production, gasoline additives compatible with the current environmental regulations [1,2]. C₅ and C₆ isoalkanes (*i*C₅ and *i*C₆) are, on the

other hand, very useful octane improvers for the gasoline pool [3].

An interesting technological alternative for the production of light isoalkanes is the isomerization/hydrocracking of long chain *n*-alkanes. Weitkamp and coworkers studied these reactions in the absence of shape-selectivity on Pt/Y zeolites [4,5] and in the presence of shape-selectivity on Pt/HZSM5 [6]. We studied the reactions using H-MOR and SO₄²⁻ promoted ZrO₂ (SZ) [7–9] as catalysts. SZ is the oxoanion promoted zirconia more extensively studied and this type of catalyst is used commercially for light alkanes isomerization [10–12]. Pt was incorporated to such catalysts to improve the stability of acid sites through the hydrogenation of unsaturated coke precursors [13,14]. The Pt/SZ catalysts have a good

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catalytic activity for isomerization and part of the SO_4^{2-} promoter is progressively reduced due to the presence of H_2 . The sulfur compounds lead to a decrease in the hydrogenating–dehydrogenation activity of Pt [9,15]. Another interesting acidity promoter is the WO_4^{2-} oxoanion. It was reported that platinum supported on tungsten oxide-promoted zirconia catalysts present a good performance for isomerization of alkanes heavier than *n*-butane (*n*C₄) [16,17]. Iglesia et al. [17] reported that, after calcination at 730–830°C and promotion with Pt, these solids catalyze C₇⁺ alkane isomerization at 130–230°C with a much higher selectivity than sulfated oxides or zeolitic acids at similar turnover rates. We studied the isomerization of *n*C₄ on $\text{WO}_3\text{-ZrO}_2$ (WZ) using ammonium metatungstate as W precursor [18], being this catalyst very active and selective. The maximum in catalytic activity per catalyst total surface area (30–45 m² g⁻¹) occurs at 15% W by weight in the catalyst. When Pt was supported on WZ obtained by different procedures [19], it was found that Pt strongly interacts with the support losing part of its metallic properties as reducibility, H₂ adsorption and dehydrogenation capacity.

The objective of this paper is the study of the hydroconversion (isomerization–cracking) of *n*-octane leading to light isoalkanes. The catalysts were SZ prepared with sulfuric acid, WZ prepared with ammonium metatungstate or tungstic acid, being these materials promoted with different Pt concentrations.

2. Experimental

2.1. Catalysts preparation

Zirconium hydroxide, Zr(OH)_4 (ZH in our nomenclature) was obtained by hydrolysis of zirconium oxychloride (Strem, 99.9998%) by addition of aqueous ammonium hydroxide up to pH = 10, then washing and drying the precipitate at 110°C overnight [20]. From this batch of ZH, three catalysts series were prepared: two promoted with tungstate and the other one promoted with sulfate.

2.1.1. Addition of WO_4^{2-} or SO_4^{2-}

WZ^{AMT}: ZH was dipped in an aqueous solution of ammonium *meta*-tungstate (AMT) ((NH₄)₆-

(H₂W₁₂O₄₀)·*n*H₂O, provided by Fluka) with a ratio: 15 ml g⁻¹ ZH. The concentration was adjusted to obtain a 15% W in the final sample. Before dipping the solid, the impregnating solution was stabilized at pH = 6 for 7 days, as recommended in [18]. The impregnation was performed under mild agitation. After 24 h at room temperature, the sample was dried at 110°C overnight. Before reaction, it was activated by calcination in air at 800°C for 3 h. The heating rate used was 12°C min⁻¹.

WZ^{TA}: ZH was impregnated to incipient wetness with an aqueous solution of tungstic acid (TA) (H₂WO₄, provided by Fluka). Due to the low solubility of the tungstic acid, diluted solutions were made and six successive impregnations were needed in order to get 15% W in the final solid. The next treatment continued as in WZ^{AMT}.

SZ: ZH was dipped in an aqueous solution (2N) of sulfuric acid (H₂SO₄) (15 ml g⁻¹ ZH) for 30 min, later filtered, dried at 110°C overnight, and calcined at 620°C for 3 h.

2.1.2. Addition of platinum

Platinum was introduced in a variable amount (0.1, 0.5 and 1%) on WZ^{AMT}, WZ^{TA} and SZ by the incipient wetness impregnation method with an aqueous solution of chloroplatinic acid (H₂Cl₆Pt·6H₂O provided by Strem). The time of impregnation was 6 h; then, the samples were dried at 110°C overnight and calcined at 500°C in an air stream for 2 h.

2.2. Catalysts characterization

2.2.1. Hydrogen adsorption and specific surface area

Hydrogen adsorption isotherms were determined to calculate the ratio H/Pt or fraction of metal exposed. Firstly, samples were heated at 300°C and reduced in hydrogen atmosphere during 1 h. Secondly, at the same temperature, they were evacuated during 2 h. The isotherms of total and irreversible hydrogen adsorption were measured at room temperature. The amount of chemisorbed hydrogen was obtained by subtracting the two isotherms, and the ratio H/Pt or metal exposition was calculated assuming dissociative adsorption of hydrogen on the Pt atoms. For the specific surface area, the catalysts samples were degassed at 200°C for 2 h, and then the nitrogen adsorption isotherm was determined at liquid nitrogen

temperature. A Micromeritics 2100 E equipment was used for both determinations.

2.2.2. Potentiometric titrations

Surface charge versus pH measurements were obtained with the usual “fast” potentiometric titration procedure on suspensions of the oxides in KNO_3 [21].

2.2.3. X-ray diffraction spectra

X-ray diffraction spectra (XRD) were recorded in a Shimadzu DX-1 spectrometer. Radiation used was $\text{Cu K}\alpha$ filtered with Ni and the 2θ scanned angle was $20\text{--}80^\circ$ at a rate of $1.2^\circ \text{ min}^{-1}$.

2.3. Activity in hydroisomerization–cracking of *n*-octane

An amount of 0.5 g of catalyst was loaded in a plug-flow reactor connected to an on-line gas chromatograph by means of a 10 loop injection valve. The reaction products were analyzed by using a 100 m capillary column coated with squalene and a FID. The test was carried out for 6 h at 300°C , 1.5 MPa, $\text{WHSV} = 4 \text{ h}^{-1}$ and a $\text{H}_2/n\text{C}_8$ molar ratio of 6. Previous to starting the run, the catalyst was kept in a hydrogen stream under reaction conditions for 2 h in order to prereduce the metallic function. $n\text{C}_8$ and other reactants were Carlo Erba PA and the hydrogen was UN45 supplied by AGA. From the chromatographic data, *n*-octane conversion and yields to the different reaction products (on a carbon basis) were calculated. The selectivity to *i* species is defined as ($10^2 \times \text{yield of } i/n\text{C}_8 \text{ conversion}$).

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows the composition and some properties of the supports and the zirconia precursor. WZ catalysts were prepared with 15 wt.% W because it was found that, at this concentration, the catalytic activity for $n\text{C}_4$ isomerization presents a maximum [18]. This concentration corresponds to $10.9 \text{ W atom nm}^{-2}$ for WZ^{AMT} and $12.3 \text{ W atom nm}^{-2}$ for WZ^{TA} . Barton et al. [22] studied the structure and catalytic activity of WO_x species supported on ZrO_2 to find that the controlling factor is the WO_x surface density (W atom nm^{-2}). The maximum in *o*-xylene isomerization turnover rates (the reaction they studied) occurs at surface densities of $8\text{--}10 \text{ W atom nm}^{-2}$, exceeding the theoretical monolayer capacity of ZrO_2 (7 W atom nm^{-2}). A large increase in activity between W concentrations corresponding to 8.6 and $9.9 \text{ W atom nm}^{-2}$ was found when we studied the influence of W concentration on $n\text{C}_4$ isomerization [18]. Considering the activity per W atom, the maximum was at a concentration of 11.5% W by weight, corresponding to a surface density of $9.9 \text{ W atom nm}^{-2}$ similar to the one of Barton et al. [22]. In our case, when increasing the W concentration from 11.5 to 15%, the activity per gram of the catalyst increases whereas the activity per W atom decreases, because some of the added W are inaccessible to reactant. The concentration of S on SZ depends on the calcination temperature, which is taken as 620°C to get the maximum in catalytic activity [20].

Table 1
Properties of the supports

Supports	Tungsten		Sulfur		Sg(BET) $\text{m}^2 \text{ g}^{-1}$	ZPC pH units	Crystalline phase of ZrO_2^{a}	Crystalline ratio WO_3/ZrO_2
	wt.%	W atom nm^{-2}	wt.%	S atom nm^{-2}				
$\text{Zr}(\text{OH})_4^{\text{b}}$	–	–	–	–	262	6.0	Amorphous	–
ZrO_2^{c}	–	–	–	–	37	5.5	20% T 80% M	–
ZrO_2^{d}	–	–	–	–	4	5.5	100% M	–
SZ ^c	–	–	1.5	2.6	110	2.0	100% T	–
$\text{WZ}^{\text{AMT}^{\text{d}}}$	14.9	10.9	–	–	45	3.2	73% T	0.13
$\text{WZ}^{\text{TA}^{\text{d}}}$	15.0	12.3	–	–	40	3.9	53% T	0.48

^a T and M represent the tetragonal and monoclinic phase.

^b Dried at 110°C .

^c Calcined at 620°C .

^d Calcined at 800°C .

Table 1 shows that the precursor $Zr(OH)_4$ without oxanion promoter and dried at 110°C has a specific surface area of $262\text{ m}^2\text{ g}^{-1}$, presenting a very weak acidity and being amorphous to XRD. The calcination of $Zr(OH)_4$ produces a large sintering, a slight increase in acidity and the crystallization mainly as monoclinic ZrO_2 . The presence of oxoanions after calcination always favors the formation of the tetragonal phase of zirconia and the stabilization of the specific surface area. Even the concentration of S is smaller than the one of W; S produces a 100% stabilization of the tetragonal phase. The WZ^{AMT} has a higher percentage of tetragonal zirconia and a smaller amount of crystallized WO_3 than WZ^{TA} . The intensity ratio of bands WO_3/ZrO_2 is based on the peaks at $2\theta = 23$ and 25° for tetragonal WO_3 , and 30.5° for tetragonal ZrO_2 in the XRD diagram.

The values of the specific surface area in both materials promoted with tungstate are similar, irrespective of using AMT or TA as W precursor. The specific surface area depends on the oxoanion used as promoter and on the calcination temperature.

The presence of Pt does not affect the specific surface area, neither the crystalline state of the supports nor these properties are affected during the 6 h catalytic run.

The zero point charge, ZPC, is a measure of acidity. $Zr(OH)_4$ is practically neutral, but the calcination in presence of the oxoanions generates acidity; SZ is a strong acid and the acidity of WZ^{AMT} is higher than the one of WZ^{TA} .

The supports without Pt do not chemisorb hydrogen and the chemisorption on Pt/SZ is negligible. For the Pt/WZ catalysts, the H/Pt ratio or fraction of metal exposed is very small for 0.1% Pt, increasing with the increment of Pt concentration. For instance, the H/Pt ratio value is 0.4 for Pt(0.1%)/ WZ^{AMT} , 9.5 for Pt(0.5%)/ WZ^{AMT} , and 66.0 for Pt(1.0%)/ WZ^{AMT} . These results are contrary to what is normally expected for Pt supported materials: to larger Pt concentrations generally corresponds a smaller dispersion or fraction of the metal exposed. This difference is due to the very strong metal-support interaction on the zirconia promoted catalysts. This interaction is more important on the catalyst with the smallest Pt content (smallest crystal size), and is the reason of the inapplicability of measuring metallic dispersion based on H_2 chemisorption. The interac-

tion of SZ on Pt is greater than the interaction of WZ.

3.2. Hydroisomerization–cracking of *n*-octane

3.2.1. Comparison of supports without metal

Fig. 1 shows the total conversion of *n*-octane (*X*) and its conversions to *n*-alkanes (C_2 , C_3 , nC_4 and nC_5) and to *i*-alkanes (iC_4 , iC_5 and iC_8) over the three acid catalysts without Pt as a function of time. In Table 2, the values of conversion and selectivities at 10, 120 and 360 min on stream are given. The evolution of total conversion on the three catalysts is similar: there is a rapid deactivation during the first 2 h and then a stabilized value is reached. The initial activity of SZ is the highest, but its stabilized value is the lowest. For the three catalysts, the main cracking products are C_3 , iC_4 , nC_4 and iC_5 , being always iC_4 the more important. During the run, the catalyst is deactivated, the cracking reactions decrease, and

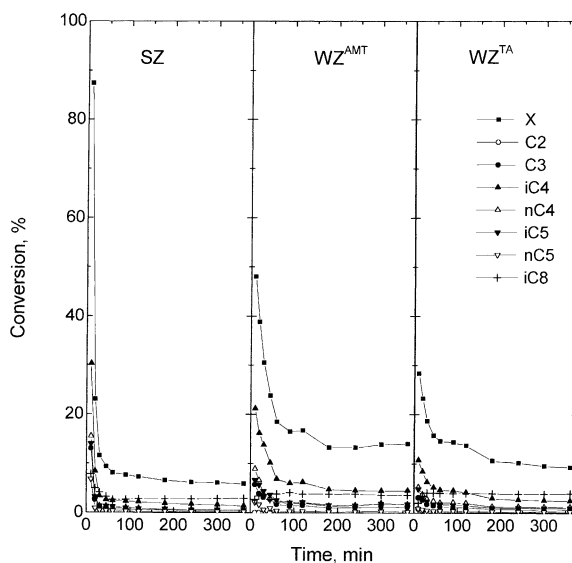


Fig. 1. Total conversion of nC_8 (*X*) and conversion to each product on SZ, WZ^{AMT} and WZ^{TA} catalysts as a function of time. Experimental conditions: 300°C , 1.5 MPa, $WHSV = 4\text{ h}^{-1}$ and molar ratio $H_2/nC_8 = 6$. Notations: SZ, sulfated zirconia; WZ^{AMT} , tungstated zirconia prepared from ammonium metatungstate; WZ^{TA} , tungstated zirconia prepared from tungstic acid; C_2 , ethane; C_3 , propane; nC_4 , normal butane; iC_4 , isobutane; nC_5 , normal pentane; iC_5 , isoalkanes of C_5 and iC_8 , isoalkanes of C_8 .

Table 2

Catalytic activity in hydroisomerization–cracking of *n*-octane of SZ, WZ^{AMT} and WZ^{TAa}

	SZ			WZ ^{AMT}			WZ ^{TA}		
	10 min	120 min	360 min	10 min	120 min	360 min	10 min	120 min	360 min
<i>X</i> (%)	87.4	7.3	5.9	48.0	16.7	13.0	28.0	13.6	9.7
<i>S</i> _{<i>n</i>P} (%)	43.1	21.0	18.6	35.0	23.0	23.6	34.0	25.6	21.2
<i>S</i> _{<i>i</i>P} (%)	55.9	74.1	81.4	64.9	76.4	76.0	64.7	73.2	77.7
<i>S</i> _{C₂} (%)	2.9	2.0	1.9	0.6	0.3	0.2	1.3	1.0	1.0
<i>S</i> _{C₃} (%)	15.9	7.8	6.6	11.9	8.8	7.8	11.1	8.2	6.4
<i>S</i> _{<i>i</i>C₄} (%)	34.5	28.6	22.5	44.1	37.1	34.2	38.3	30.6	26.2
<i>S</i> _{<i>n</i>C₄} (%)	17.6	10.6	8.9	18.5	12.0	11.1	18.6	14.5	12.1
<i>S</i> _{<i>i</i>C₅} (%)	16.6	9.9	8.6	13.9	12.5	11.4	16.7	11.2	10.0
<i>S</i> _{<i>n</i>C₅} (%)	7.0	2.7	2.3	4.4	1.7	1.6	3.9	2.5	2.3
<i>S</i> _{<i>i</i>C₆} (%)	–	–	–	0.9	2.6	2.9	1.4	1.3	0.8
<i>S</i> _{<i>n</i>C₆} (%)	–	–	–	0.1	0.4	0.5	1.1	0.3	0.2
<i>S</i> _{<i>i</i>C₇} (%)	–	–	–	0.4	1.4	1.3	0.4	0.6	0.6
<i>S</i> _{<i>n</i>C₇} (%)	–	–	–	0.1	0.2	0.2	0.1	0.1	0.3
<i>S</i> _{<i>i</i>C₈} (%)	5.4	35.6	47.2	5.6	22.8	28.5	7.0	29.4	40.1

^a Values of total conversion (*X*) and selectivities (*S*) at three times-on-stream. Reaction conditions: 300°C; 1.5 MPa; molar ratio H₂/*n*C₈ = 6 and WHSV = 4 h⁻¹. *S*_{*n*P}: selectivity to normal alkanes with lower than eight carbon atoms; *S*_{*i*P}: selectivity to all the isoalkanes produced; *S*_{C₂}: selectivity to ethane; *S*_{C₃}: selectivity to propane; *S*_{*i*C_{*m*}}: selectivity to *i*-alkane of *m* carbon atoms; *S*_{*n*C_{*m*}}: selectivity to *n*-alkane of *m* carbon atoms.

the production of *i*C₈ increases. This means that *i*C₈ is an intermediate: *n*C₈ isomerizes to *i*C₈ which is then cracked. The *S*_{*n*P} is the selectivity to *n*-alkanes produced by cracking. Also, *S*_{*i*P} is the selectivity to *i*-alkanes obtained by isomerization (*i*C₈) and by isomerization–cracking (*i*C₄ to *i*C₇). During the run, *S*_{*n*P} decreases because of the decrease in cracking reaction. The increase in *S*_{*i*P} is mainly due to the increase in *i*C₈ production, because *S*_{*i*C₄} and *S*_{*i*C₅} are decreased.

The selectivity ratio *i/n* for C₄ and C₅ gives an idea of the ratio isomerization/cracking, being higher on WZ than on SZ. The ratio increases during the run, mainly in SZ due to its higher deactivation, which decreases cracking and allows more isomerization of the adsorbed C₈ carbenium ion species. The iso to normal C₄ and C₅ ratios are higher than the ones of the thermodynamic equilibrium of isomerization of normal to isoalkane. Therefore, *i*C₄ and *i*C₅ are not produced by isomerization of *n*C₄ or *n*C₅ already produced by cracking, but they are produced by cracking of *i*C₈. The isomerization rate of the produced C₄ and C₅ alkanes is very low compared to *i*C₈ cracking, and the isomerization equilibrium value is not approached. The intermediate *i*C₈ carbenium ion adsorbed on the catalyst surface that is cracked would have to be multi-

branched, because cracking of monobranched *i*C₈ will produce lower *i* to *n* ratios than the ones found experimentally. Weitkamp et al. [6] stated that carbenium ion chemistry favors the formation of tertiary fragments, precursors of *i*C₄, over the formation of secondary or primary ion fragments, precursors of *n*C₄.

The SZ has the highest cracking activity and WZ^{TA} the lowest one, which agrees with the highest acidity value of SZ shown in Table 1. The high acidity of SZ is also the reason of its rapid deactivation by production of carbonaceous deposits catalyzed by the acid sites. The concentration of S is lower than the one of W (Table 1); nevertheless, S produces a more active material. On SZ there is not C₆ and C₇ production, and the selectivities to C₂ and C₃ are higher than on WZ because the higher acidity of SZ catalyzes the cracking of C₆ and C₇.

WZ^{AMT} is more active than WZ^{TA} because of the higher acidity (Table 1) and the better WO_x distribution on the zirconia surface with a smaller fraction of W in the form of WO₃ crystals (Table 1, ratio of intensities WO₃/ZrO₂ in DRX). This statement is in agreement with the literature stating that the best catalyst is the one with a very high WO_x dispersion and with a W concentration just before the start of WO₃ crystallization [17–19].

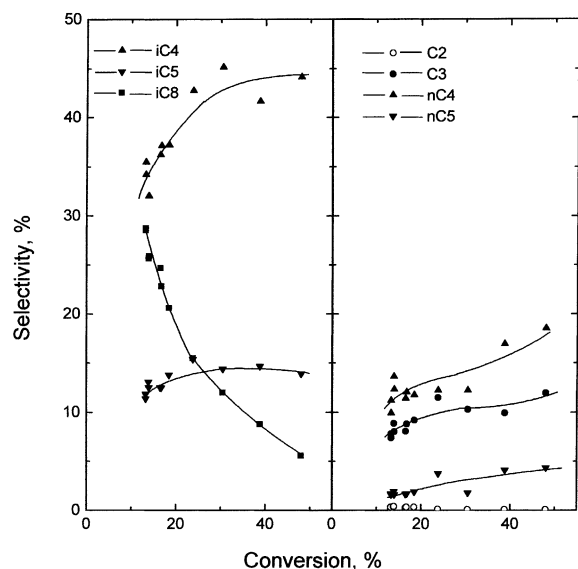


Fig. 2. Selectivity of each product as a function of total conversion of nC_8 on WZ^{AMT} catalyst. Experimental conditions and notations: the same as in Fig. 1.

Under our experimental conditions, SZ shows the highest cracking activity due to its strong acidity, which is rapidly deactivated. WZ^{AMT} is the best catalyst for iC_4 production because of its cracking and isomerization activities, and WZ^{TA} is the best for the production of iC_8 because of its weaker

acidity better able for isomerization than for cracking.

Fig. 2 shows the selectivity to each product as a function of total conversion of nC_8 , on WZ^{AMT} catalyst. The cracking products yield decreases with the decrease in nC_8 conversion, while the yield of the intermediate iC_8 increases, increasing greatly the selectivity to iC_8 .

Regarding the reaction mechanism that justify the results, the reactions are governed by carbenium ion chemistry. nC_8 is adsorbed on the acid surface where octyl carbenium ions are formed. These ions can rearrange producing branched octyl carbenium ions, which after hydride ion incorporation can be desorbed as iC_8 or after β -scission and hydride incorporation can produce light alkanes. The selectivity between the reactions of isomerization and cracking is mainly fixed by the lifetime of the carbenium ions. Stronger acid sites will produce a longer lifetime of the ions, and therefore, more possibility of cracking.

3.2.2. Comparison of supports with metals

Tables 3–5 give values of nC_8 conversion and selectivities at 10, 120 and 360 min time on stream for each acid support and for three Pt contents. The addition of Pt to the supports produces an increase in catalytic activity and a large increase in stability. This can be clearly seen in Fig. 3, where the total nC_8 conversion and its conversions to the main products are shown

Table 3

Catalytic activity in hydroisomerization–cracking of n -octane of Pt/SZ with different metallic loads, 0.1, 0.5 and 1%^a

	Pt(0.1%)/SZ			Pt(0.5%)/SZ			Pt(1%)/SZ		
	10 min	120 min	360 min	10 min	120 min	360 min	10 min	120 min	360 min
X (%)	99.9	91.7	89.8	94.6	80.9	80.6	91.9	76.4	75.7
S_{nP} (%)	49.1	47.1	44.8	48.2	41.4	40.4	45.7	39.3	38.9
S_{iP} (%)	50.9	52.9	55.2	51.8	58.6	59.6	54.3	60.7	61.1
S_{C_2} (%)	1.2	0.6	0.5	1.0	0.3	0.2	0.4	0.2	0.1
S_{C_3} (%)	20.3	17.6	16.9	19.0	17.6	16.4	16.7	14.5	14.7
S_{iC_4} (%)	34.9	34.6	34.1	34.0	35.4	34.8	33.2	33.3	31.9
S_{nC_4} (%)	20.1	20.9	20.2	20.3	17.4	18.1	20.1	18.3	18.5
S_{iC_5} (%)	15.8	15.9	16.2	15.6	16.5	16.6	17.4	16.3	16.6
S_{nC_5} (%)	7.6	7.6	7.1	7.9	6.1	5.6	8.5	6.4	5.6
S_{iC_6} (%)	–	–	–	–	–	–	–	–	–
S_{nC_6} (%)	–	–	–	–	–	–	–	–	–
S_{iC_7} (%)	–	–	–	–	–	–	–	–	–
S_{nC_7} (%)	–	–	–	–	–	–	–	–	–
S_{iC_8} (%)	0.2	1.9	4.3	2.1	6.6	8.2	3.8	11.0	12.4

^a Values of total conversion (X) and selectivities (S) at three times-on-stream. Reaction conditions as in Table 2.

Table 4

Catalytic activity in hydroisomerization–cracking of *n*-octane of Pt/WZ^{AMT} with different metallic loads, 0.1, 0.5 and 1%^a

	Pt(0.1%)/WZ ^{AMT}			Pt(0.5%)/WZ ^{AMT}			Pt(1%)/WZ ^{AMT}		
	10 min	120 min	360 min	10 min	120 min	360 min	10 min	120 min	360 min
<i>X</i> (%)	62.7	56.3	55.4	56.9	50.7	50.1	56.0	50.1	48.9
<i>S</i> _{nP} (%)	38.9	36.3	34.7	36.8	33.0	29.4	35.9	27.9	24.3
<i>S</i> _{iP} (%)	61.1	63.6	65.2	63.2	67.0	70.6	64.1	72.1	75.7
<i>S</i> _{C₂} (%)	0.3	0.2	0.2	0.7	0.3	0.2	0.7	0.2	0.1
<i>S</i> _{C₃} (%)	13.5	12.9	12.6	13.9	11.8	10.0	13.1	9.6	8.1
<i>S</i> _{iC₄} (%)	44.3	43.5	43.6	43.2	36.4	35.9	38.6	27.9	25.9
<i>S</i> _{nC₄} (%)	19.9	18.1	17.5	16.1	17.2	15.7	16.8	14.8	12.9
<i>S</i> _{iC₅} (%)	15.2	13.1	13.0	12.6	12.8	12.4	12.6	11.9	10.2
<i>S</i> _{nC₅} (%)	5.2	4.6	4.0	5.7	3.8	3.3	5.3	3.2	3.1
<i>S</i> _{iC₆} (%)	–	1.2	1.1	–	0.3	0.2	–	–	0.1
<i>S</i> _{nC₆} (%)	–	0.4	0.4	–	0.1	0.1	–	–	–
<i>S</i> _{iC₇} (%)	–	0.2	0.2	–	–	0.1	–	–	–
<i>S</i> _{nC₇} (%)	–	0.1	0.1	–	–	–	–	–	–
<i>S</i> _{iC₈} (%)	1.7	5.6	7.2	7.3	17.5	22.1	12.8	32.3	39.5

^a Values of total conversion (*X*) and selectivities (*S*) at three times-on-stream. Reaction conditions as in Table 2.

for each acid support when promoted with 0.1% Pt. There is no production of C₁, then hydrogenolysis on Pt sites can be discarded. For each support, the increase in the concentration of Pt produces a decrease in *n*C₈ conversion together with a decrease in *i*C₄ selectivity (cracking product) and an increase in *i*C₈ selectivity. Similarly to the supports without Pt, Pt/WZ produces more isomers than Pt/SZ. Pt(1%)/WZ^{TA} has the smallest *n*C₈ conversion, the lowest cracking ac-

tivity and the largest production of *i*C₈. When adding Pt to the supports, the ratio *i/n* decreases for both C₄ and C₅. At 10 min, the value of *i*C₄/*n*C₄ is 2 for SZ and decreases to 1.7 when adding 0.1% Pt, *i*C₅/*n*C₅ decreases from 2.4 to 2.1. For WZ^{AMT}, the ratio values of C₄ and C₅ are 2.4 and 3.2 and decrease to 2.2 and 2.9 respectively when adding Pt. For WZ^{TA}, the ratio values are 2.1 and 4.3 and with 0.1% Pt decrease to 1.8 and 2.2, respectively. For each support the

Table 5

Catalytic activity in hydroisomerization–cracking of *n*-octane of Pt/WZ^{TA} with different metallic loads, 0.1, 0.5 and 1%^a

	Pt(0.1%)/WZ ^{TA}			Pt(0.5%)/WZ ^{TA}			Pt(1%)/WZ ^{TA}		
	10 min	120 min	360 min	10 min	120 min	360 min	10 min	120 min	360 min
<i>X</i> (%)	48.1	39.3	35.4	46.9	37.7	33.9	32.8	27.8	27.9
<i>S</i> _{nP} (%)	40.9	28.7	25.5	35.4	23.3	19.1	23.3	7.7	5.8
<i>S</i> _{iP} (%)	59.1	71.3	74.5	64.6	76.6	80.9	76.7	92.3	94.2
<i>S</i> _{C₂} (%)	0.6	0.4	0.4	0.4	0.3	0.2	0.4	0.2	0.1
<i>S</i> _{C₃} (%)	13.0	10.7	8.4	12.0	7.2	5.9	11.1	2.2	1.7
<i>S</i> _{iC₄} (%)	36.3	32.0	29.7	34.0	25.1	22.1	18.3	8.0	6.4
<i>S</i> _{nC₄} (%)	20.3	14.1	13.8	18.2	11.9	10.1	8.8	3.9	3.0
<i>S</i> _{iC₅} (%)	15.2	13.8	12.9	12.8	8.4	7.0	7.0	3.5	2.7
<i>S</i> _{nC₅} (%)	6.9	3.5	2.8	4.7	3.7	2.8	3.0	1.4	0.9
<i>S</i> _{iC₆} (%)	0.1	0.2	0.1	0.7	0.6	0.3	–	–	–
<i>S</i> _{nC₆} (%)	–	0.1	0.1	0.1	0.2	0.1	–	–	–
<i>S</i> _{iC₇} (%)	–	–	–	–	0.2	0.1	–	–	–
<i>S</i> _{nC₇} (%)	–	–	–	–	0.1	0.1	–	–	–
<i>S</i> _{iC₈} (%)	7.5	25.3	31.8	17.1	42.4	51.5	51.5	80.8	85.2

^a Values of total conversion (*X*) and selectivities (*S*) at three times-on-stream. Reaction conditions as in Table 2.

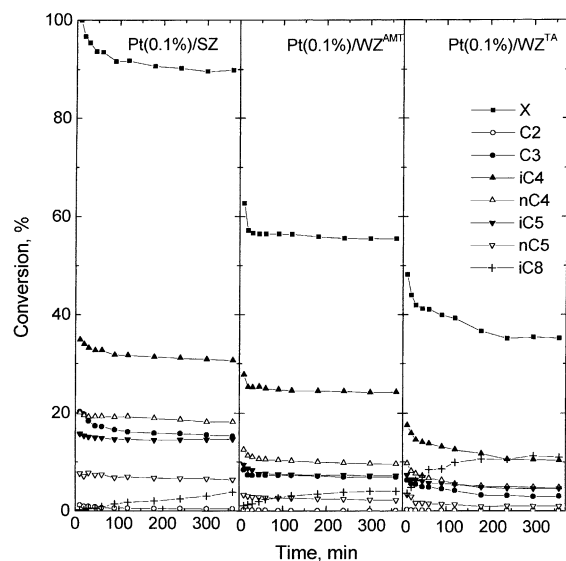


Fig. 3. Total conversion of nC_8 and conversion to each product on the three supports with addition of 0.1% Pt as a function of time. Experimental conditions and notations: the same as in Fig. 1.

ratios are similar for the three Pt contents and, in spite of a decrease in these products of cracking, the ratios remain practically constant during the run. To the highest nC_8 conversion corresponds the smallest production of the intermediate iC_8 .

Table 6 shows the distribution of the C_8 isoalkanes produced by the catalysts at 360 min time on stream. On the supports without Pt, those with a lower acid-

ity (WZ) produce a larger yield to iC_8 , mainly by the formation of monobranched isomers. The production of iC_8 increases with the addition of 0.1% Pt and with the increment in Pt concentration, being the di- and tribranched isomers mainly increased. Particularly, the catalyst Pt(1%)/WZ^{TA} has a 14.6% selectivity to dimethylhexane and a 8.5% selectivity to trimethylpentane, which is attractive because of the high octane number of these branched compounds. The increase in iC_8 production is due to the decrease of cracking produced by the presence of Pt.

The Pt supported catalysts can be considered as metal–acid bifunctional catalysts. To have the advantages of this type of catalysts, the simultaneous presence of Pt and H_2 is necessary. This is verified by the runs shown in Fig. 4. Using the supports SZ and WZ^{AMT} and with H_2 as carrier of nC_8 , the catalytic activity drops rapidly in the first hour on stream, keeping then a stabilized value (curves c and c'). When 0.1% Pt is added to the supports and with H_2 as carrier, there is an increase in conversion, the deactivation is smaller and a stabilization value higher than that of the former experiments is reached (curves a and a'). The catalysts with 1% Pt and H_2 (curves b and b') also show the beneficial effect of Pt, although in a lower extent than the one of the 0.1% Pt catalysts. With the 1% Pt catalysts and using He instead of H_2 as carrier (curves d and d'), the catalysts are unstable with a rapid deactivation and reaching a stabilized activity lower than that in the case of using H_2 . This shows that Pt and H_2 must be simultaneously present to have

Table 6

Total conversion (X) and yield to each C_8 isomer (Y) produced on the catalysts by n -octane reactions at 360 min on-stream^a

Catalysts	X (%)	Y_{2MC_7}	Y_{3MC_7}	Y_{DMC_6}	Y_{TMC_5}	$Y_{iC_8}^{Total}$
SZ	5.9	0.95	1.41	0.42	–	2.78
Pt(0.1%)/SZ	89.8	1.29	1.33	0.84	0.39	3.84
Pt(0.5%)/SZ	80.6	2.25	2.33	1.33	0.73	6.64
Pt(1.0%)/SZ	75.7	3.54	3.21	1.54	1.09	9.39
WZ ^{AMT}	13.0	1.21	2.03	0.38	0.05	3.67
Pt(0.1%)/WZ ^{AMT}	55.4	0.87	1.69	0.95	0.50	3.99
Pt(0.5%)/WZ ^{AMT}	50.1	3.99	4.34	1.43	1.29	11.07
Pt(1.0%)/WZ ^{AMT}	48.9	7.40	6.95	2.94	2.03	19.32
WZ ^{TA}	9.7	1.15	2.23	0.40	0.11	3.89
Pt(0.1%)/WZ ^{TA}	35.4	3.87	4.80	2.38	0.21	11.26
Pt(0.5%)/WZ ^{TA}	33.9	6.43	6.82	3.28	0.94	19.10
Pt(1.0%)/WZ ^{TA}	27.9	7.84	9.55	4.06	2.37	23.83

^a M: methyl; DM: dimethyl; TM: trimethyl. Reaction conditions shown in Table 2.

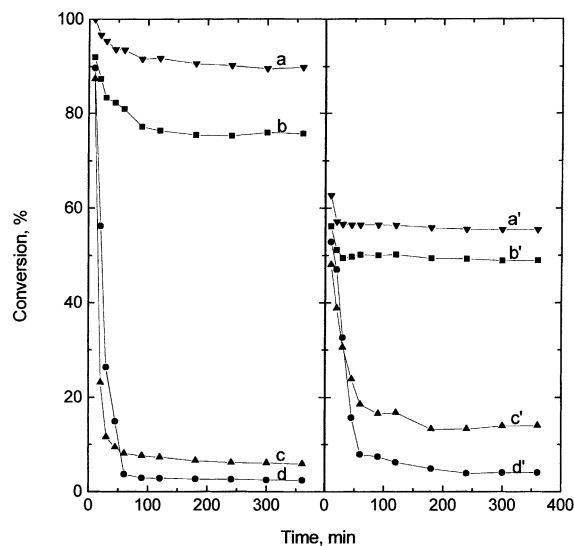


Fig. 4. Total conversion of nC_8 as a function of time on SZ and WZ^{AMT} with or without Pt and with H_2 or He as carrier gas. (a) Pt(0.1%)/SZ, H_2 ; (b) Pt(1%)/SZ, H_2 ; (c) SZ, H_2 ; (d) Pt(1%)/SZ, He; (a'), Pt(0.1%)/ WZ^{AMT} , H_2 ; (b') Pt(1%)/ WZ^{AMT} , H_2 ; (c') WZ^{AMT} , H_2 ; (d') Pt (1%)/ WZ^{AMT} , He. The same experimental conditions as in Fig. 1.

the advantages of bifunctionality. Pt in the presence of H_2 hydrogenates coke precursors keeping a stable catalytic activity. Pt without H_2 has no beneficial effects. In this case, the deactivation is even higher than in the case of SZ and WZ^{AMT} , because Pt acts as a dehydrogenation catalyst, producing small amounts of alkenes and aromatics that form more condensed carbonaceous deposits on the catalyst.

The main action of Pt and H_2 in these catalysts is to greatly increase the stability, with smaller changes in activity and selectivity. This action is different to the one on the classical bifunctional catalyst; for example, Pt on protonic mordenite [7]. For the nC_8 reaction under similar conditions to the ones of this paper, when 0.3% Pt is added to H-MOR, the conversion increases from 18.2% for H-MOR to 80% and also the selectivity to isomers and the stability are increased. The reason of the different behavior of the catalysts Pt/promoted zirconia is that the metallic function of Pt is greatly decreased due to its strong interaction with the support. The small action of Pt is not enough to generate an important contribution of the bifunctional mechanism of reaction to the only acid mechanism,

and also is not enough to produce sufficient generation and spillover of dissociated hydrogen from Pt to the support in order to modify the reaction intermediates disfavoring the ones that produce cracking. The small hydrogen spillover is enough to hydrogenate coke precursors because the reaction rate of coking is very low compared to the main reactions. Barbier [23] stated that only one atom of carbon out of 200,000 activated by the catalyst is transformed into carbonaceous deposit; then, a small amount of activated hydrogen is enough to stop this transformation.

There are many references in the literature regarding this strong metal support interaction in Pt/SZ. Pt cannot be completely reduced to Pt^0 , cationic Pt atoms were found by XPS and EXAFS [24,25]. These Pt atoms have poor or null properties for hydrogen chemisorption and hydrocarbon hydrogenation–dehydrogenation [26].

A layer of Pt oxidized species on the surface of a Pt^0 core has been proposed as a model for the Pt particle supported on SZ [25]. Regarding Pt/WZ, Contreras et al. [27] reported that the addition of W^{6+} to 0.3% Pt/ Al_2O_3 modifies both reducibility and chemisorption capacity of Pt, presumably due to a strong interaction with the oxide precursors. Regabulto et al. [28] reported a decrease in CO chemisorption upon the introduction of WO_3 to Pt/ SiO_2 . They stated that decoration of Pt by WO_x species produces a physical blockage of the metallic sites. Contreras and Fuentes [29] proposed that W induces electronic and/or steric modifications of Pt particles.

It is interesting that, in these oxoanion promoted zirconia catalysts, the increase in Pt concentration produces a decrease in the acid activity (cracking) of the catalyst. Keogh et al. [30], studying the hydroisomerization and hydrocracking of n -hexadecane on Pt/SZ, found that small additions of Pt to SZ produce an increase in the activity, and that further increases in the Pt concentration cause a decrease in conversion. Similarly, Hino and Arata [31], changing the Pt concentration on Pt/SZ, found a maximum in isomerization of nC_4 . Regarding Pt/WZ, Santiesteban et al. [32] showed Pt has a deleterious effect on the high acidity of WO_x - ZrO_2 catalysts by facilitating tungsten reduction. Hoang-Van and Zegaoni [33], studying Pt/ WO_3 , found that in the presence of H_2 , bronzes (H_2WO_3) are produced. This is due to the partial reduction of WO_3 by H_2 spilled over from Pt. These results show

a similarity with our results: high Pt concentrations produce deactivation of the acid function of the catalyst. This behavior is different to the one of the classical Pt supported bifunctional catalysts. For instance, the classical paper of Sinfelt et al. [34] on nC_7 isomerization over Pt/Al₂O₃ shows that Al₂O₃ alone is not active, the addition of Pt produces an active catalyst and, for Pt contents larger than 0.1%, the conversion becomes independent of Pt content. For 0.1% Pt, sufficient active metal surface area is present to provide the equilibrium concentration of alkenes, and the isomerization on the Al₂O₃ acid sites becomes the rate-limiting step. Similarly, in the hydroisomerization of nC_7 and hydroisomerization–hydrocracking of nC_{10} on Pt/zeolite, the activity of the zeolite increases with the addition of Pt [35,36] and, from a certain Pt concentration, the activity remains constant, independent of the Pt content and depending only on the acidity of the zeolite. Also, Sinfelt et al. [34] stated that the activity of Pt for dehydrogenation of methylcyclohexane to toluene on Pt/Al₂O₃ is proportional to the Pt content over the whole range of concentration used by them, independently whether the isomerization was controlled by the metal or the acid function. These references show that there is a synergetic action between the metal and the acid functions in the classical bifunctional mechanism, but each function has always its full catalytic activity.

The behavior is completely different on the bifunctional Pt-oxoanion promoted zirconia catalysts: the metallic activity of Pt is greatly decreased due to its strong interaction with the support, and the acid activity of the support is also decreased due to the presence of Pt. The maximum in activity found by several authors [30,31] could be a compensation between the increase caused by the operation of a bifunctional mechanism and the decrease caused by the deactivating action of Pt.

4. Conclusions

Zirconia promoted with sulfate or with tungstate are active catalysts for the hydroconversion (isomerization–cracking) of n -octane. The more acid catalyst (SZ) is the more active, the less stable and the one with more cracking compared to isomerization. The isomerization of nC_8 to iC_8 and the isomerization–cracking

to iC_4 and iC_5 are higher on WZ. The addition of 0.1% Pt to both kinds of catalysts produces an increase in catalytic activity (conversion) and, proportionally, a larger increase in stability. Further increase in Pt concentration produces the deactivation of the catalysts, mainly on the cracking reactions (leading to iC_4 and iC_5) increasing the iC_8 production.

The Pt/promoted zirconia is a particular kind of bifunctional catalysts showing a behavior different to the one of the classical bifunctional metal–acid catalysts. This difference is due to the strong metal–support interaction; the metallic properties of Pt are decreased by the oxoanion promoted zirconias and the cracking activity of these supports is decreased by the presence of Pt. The strong acidity (for cracking) is mainly decreased by Pt. Because of this behavior, the contribution of the bifunctional mechanism of reaction to the only acid mechanism is small, being also small the modification of carbenium ion reactions selectivity whereas the more important contribution of Pt is found in the increasing stability.

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