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Comparison between Ni and Pt promoted SO_4^{2-}–ZrO_2 catalysts for *n*-octane hydroisomerization-cracking

J.C. Yori, J.M. Grau, V.M. Benítez, C.R. Vera, C.L. Pieck, and J.M. Parera

Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FIQ-UNL, CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

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The production of C_4–C_6 branched isoalkanes by isomerization-cracking of *n*-octane (300 °C, 0.1 MPa) using sulfated zirconia catalysts was studied. The effect of Ni addition on the activity and selectivity was compared to the effect of Pt. Pt enhanced the activity and stability of the catalysts. Ni mainly improved the selectivity to isoparaffins (maximum yield at 1% Ni). *n*-Octane conversion fully correlated with total acidity. Average and final stable conversion values were in comparison lower for Ni catalysts. This result was addressed to the lower metal activity of Ni and to the detrimental effect of sulfated zirconia on the reducibility of the metal.

KEY WORDS: sulfated zirconia; hydroisomerization; hydrocracking; *n*-octane.

1. Introduction

Hydrocracking has been practiced in modern oil refineries for the production of light fuels from heavy distillate and residua since 1959 when Chevron announced its Isocracking process. Hydroisomerization and hydrocracking cost-effectively convert medium- to heavyweight cuts into high-value streams, like gasoline and jet fuel, other middle distillates and lube oils. Waxy compounds, chiefly normal-paraffins, are however largely unaffected and must be removed in a subsequent process in order to reduce the pour point.

The conversion of long normal-paraffins into branched ones boiling in the naphtha range (C_5–C_7) by means of hydroisomerization-cracking has received growing attention in the last years [1–6]. Conversion of long paraffins has been studied mainly on Pt-doped zeolites but lately the attention has been focused on the use of bifunctional superacid catalysts [7–11], composed of a zirconium oxide support surface promoted with sulfate or WO_3. The metal function needed for hydrogenation/dehydrogenation is provided by a Group VIII metal, e.g. Pt. These catalysts conveniently provide high activity at low temperatures, thermodynamically favouring the conversion to isoparaffins.

Sulfated zirconia (SO_4^{2-}–ZrO_2) has proved to be more active than tungsten–zirconia (WO_3–ZrO_2) while the latter has proved to be more selective to hydroisomerization products. In both catalysts the interaction between the metal function and the support is very strong and is seemingly related to the crystalline state of the zirconia support [12,13]. Pt is present both as zerovalent Pt^0 and as electron deficient $Pt^{\delta+}$.

The use of Ni other than Pt in oxoanion promoted catalysts for hydroisomerization-cracking has been reported [9] but not studied thoroughly. Both Ni and SO_4^{2-} or WO_3 promoted ZrO_2 have been used in *n*-butane isomerization and ethylene dimerization [14–16].

The role of Ni in Ni/SO_4^{2-}–ZrO_2 catalysts for the hydroconversion of long paraffins is studied in this work and *n*-octane is used as model molecule. The performance of Ni/SO_4^{2-}–ZrO_2 catalysts is compared to that of Pt/SO_4^{2-}–ZrO_2 catalysts.

2. Experimental

2.1. Catalysts preparation

Zirconium hydroxide, $Zr(OH)_4$, was obtained by hydrolysis and precipitation of zirconium oxychloride (Strem, 99.9998%) [17]. To obtain zirconia, ZrO_2, $Zr(OH)_4$ was calcined at 620 °C for 3 h in flowing air (10 mL min^{-1}). A γ-Al_2O_3 support was obtained from Ketjen (CK300, 180 m^2/g) and stabilized by calcination in flowing air (10 mL min^{-1}) for 3 h at 450 °C.

Sulfated zirconium hydroxide, was prepared by incipient wetness impregnation of $Zr(OH)_4$ with a volume of H_2SO_4 2 N equal to the pore volume plus a 10% excess (0.4 mL/g). The material was then dried at 120 °C overnight. Sulfated zirconia, SO_4^{2-}–ZrO_2 (SZ sample), was finally obtained by calcination in an air flow (10 mL min^{-1}) at 620 °C for 3 h.

γ-Al_2O_3 and SO_4^{2-}–ZrO_2 (all ground to 35–80 mesh) were impregnated by incipient wetness, using $Ni(NO_3)_2 \cdot 6H_2O$ aqueous solutions. The concentration

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*To whom correspondence should be addressed.
E-mail: jyori@fiqus.unl.edu.ar

of the impregnating solutions was adjusted in order to obtain catalysts with different Ni contents (0.1, 0.5, 1.0 and 5%). The catalysts were then dried at 120 °C overnight. Before the reaction test the catalysts were calcined in an air flow (10 mL min^{-1}) for 3 h at 450 °C. The catalysts thus obtained were called 0.1, 0.5, 1.0 and 5.0Ni/SZ (SO_4^{2-}–ZrO_2 supported Ni), 1.0 and 5.0Ni/A (γ-Al_2O_3 supported Ni).

Portions of the γ-Al_2O_3 and SO_4^{2-}–ZrO_2 batchs were impregnated with solutions of chloroplatinic acid and calcined in the same way as the Ni catalysts. Catalysts with x% Pt (x = 0.1, 0.5, 1.0 and 5.0) were obtained (xPt/A and xPt/SZ catalysts).

2.2. Characterization

Hydrogen adsorption isotherms were taken in order to calculate the dispersion of the Pt and Ni metal particles. The specific surface area was measured by nitrogen adsorption at the temperature of liquid nitrogen after degassing in vacuo at 200 °C for 2 h. A Micromeritics 2100E equipment was used for both H_2 and N_2 adsorption measurements.

Temperature programmed reduction tests were performed in an Ohkura TP-2002-S apparatus. X-ray diffraction spectra were recorded in a Shimadzu DX-1 spectrometer.

The amount of acid was assessed by means of temperature programmed desorption of pyridine. The apparatus and technique used have been described elsewhere [12].

2.3. Reaction tests

Cychlohexane dehydrogenation of benzene was chosen for assessing the dehydrogenating capacity of the supported Pt and Ni particles. The catalyst was loaded in a glass reactor, heated from room temperature to 300 °C in 2 h and kept at this temperature for 1 h in flowing hydrogen (30 mL min^{-1}). Then the reaction was performed at 300 °C, 0.1 MPa, catalyst mass = 0.1 g, WHSV = 10 h^{-1} and $H_2/C_6H_{12}=30$ (molar ratio).

Isomerization-cracking of n-octane: an amount of catalyst in order to keep a constant mass of 0.5 g of SO_4^{2-}–ZrO_2 in each test was loaded in a plug-flow reactor connected to a on-line gas chromatograph. Reaction conditions were: temperature = 300 °C, pressure = 1.5 MPa, WHSV = 4 h^{-1}, molar ratio $H_2/n\text{-}C_8=6$, total time-on-stream = 10 h. Before the reaction the catalysts were heated from room temperature to 300 °C in hydrogen (2.3 °C min^{-1} heating rate) and kept for 1 h at 300 °C and 1.5 MPa. n-C_8 was Carlo Erba pro analysis. Hydrogen was supplied by AGA. The selectivity to normal alkanes lower than eight carbon atoms, $S_{n\text{-}P}$, was taken as a representative of the hydrocracking selectivity. Selectivity to iso-alkanes, $S_{i\text{-}P}$, including all the iso-alkanes produced, was taken as the hydroisomerization selectivity.

3. Results and discussion

$Zr(OH)_4$ without sulfate and dried at 110 °C had a specific surface area of 262 m^2 g^{-1} and was XRD amorphous. The calcination at 600 °C of $Zr(OH)_4$ produced extensive sintering and the sample crystallized mainly as monoclinic ZrO_2. The presence of surface sulfate inhibited crystallization, favored the formation of the tetragonal phase of zirconia and stabilized the specific surface area. The final S contents were 1.6–2.0%. SO_4^{2-}–ZrO_2 samples were mainly tetragonal and their crystallinity was lower than that of ZrO_2. In the case of the sulfated zirconia catalysts, the presence of Ni or Pt did not affect the specific surface area or the crystal phase of the support. These samples were almost completely tetragonal and their area was 110–120 m^2/g.

Figure 1 contains the results of the TPR tests performed on catalysts of varying Ni content. When deposited over alumina the reduction of Ni occurs in the 200–800 °C range with 4 peaks at 249 (shoulder), 319, 642 and 828 °C. In the case of the 1.0Ni/A catalyst the first two peaks are the most important ones. Whenever Ni is deposited over SZ, hydrogen is consumed between 400 and 600 °C and uptake peaks at 249 °C and 319 °C disappear. This consumption corresponds both to the reduction of Ni and to the reduction of sulfate to SO_2 and elemental sulfur [18]. As with Pt/SZ, interaction between Ni and SZ shifts the onset of metal reduction to higher temperatures. From this we conclude that at the reaction temperature (300 °C) Ni is mainly oxidized.

The supports without Pt or Ni did not chemisorb hydrogen. 1.0Ni/A reduced at 300 °C had a value of H/Ni = 0.2 while for all the Ni/SZ catalysts reduced at

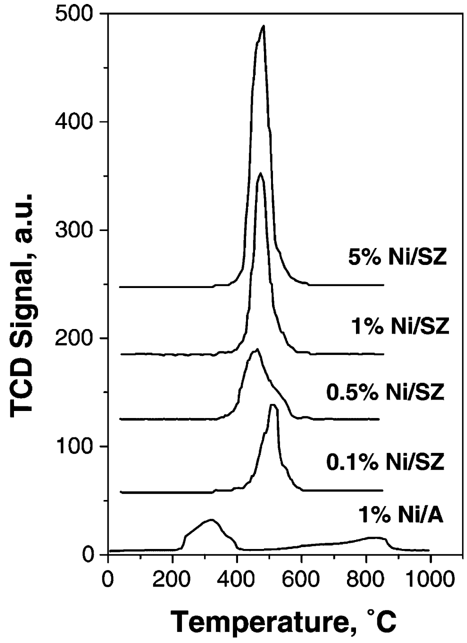

Figure 1. Temperature programmed reduction results.

this temperature the chemisorption was practically nil. For the Pt/SZ catalysts, hydrogen uptake was very low (0.1Pt/SZ: H/Pt = 0.015; 0.5Pt/SZ: H/Pt = 0.046; 1.0Pt/SZ: H/Pt = 0.067). The decreased chemisorption capacity in the case of Pt can be explained by the combined effect of sulfur poisoning and a strong metal-support interaction between Pt and SO_4^{2-}–ZrO_2 [12].

Cyclohexane conversion on all Ni/SZ catalyst was practically zero. The maximum activity (conversion at 1 h time-on-stream) was displayed by the 1.0Pt/SZ catalyst (7.3% conversion) and the Ni/A catalysts (11% for 1.0Ni/A and 17% for 5.0Ni/A). The results clearly confirm that supporting Ni over sulfated-zirconia inhibits its metal properties and that the metal is oxidized even after reduction at 300 °C. Higher reduction temperatures cannot be employed because they would produce the removal of most surface sulfates and the irreversible deactivation of the catalyst [8].

Table 1 shows the results of the TPD of pyridine. Ni addition decreases the total amount of acid sites. This effect is more pronounced in the Ni/SZ catalyst of lowest Ni content (0.1%). In this catalyst about 11 acid sites are neutralized for each atom of Ni added. Similar results have been recently reported by Carvalho *et al.* [19], indicating that Sn addition to chlorided alumina neutralizes 10 acid sites per Sn atom. The multiple neutralization occurring upon addition of small amounts of promoter can be attributed to the simultaneous direct neutralization of very strong acid sites and the indirect neutralization of other weaker acid sites in the neighbourhood which had been formed by polarization of the lattice by the electrophillic anion (Cl^-, SO_4^{2-}) associated to the strong acid site. The relative decrease of the acidity is milder at higher Ni contents and a progressive increase in acidity is obtained after the initial decrease upon Ni loading. The same effect has been reported by Perez *et al.* [20] who found that 4.5% Ni/SO_4^{2-}–ZrO_2 had practically the same total acidity as Ni free SO_4^{2-}–ZrO_2 while the catalysts with lower Ni content had lower acidity. Barrio *et al.* [21] found that Ni addition to acidic silica–alumina decreased its acidity to 59% its original value with 4% Ni and to 65% with 8% Ni, while the original strong acid sites disappeared, being neutralized and converted to weak and mildly strong ones. The formation of surface nickel aluminates and its effect in increasing the net positive charge of the surface coordinatively unsaturated sites has been proposed in order to rationalize the influence of nickel on increasing the acid strength of amphoterous *g*-alumina [22]. Rodríguez-Castellón *et al.* [23] have found that Ni addition to SiO_2–ZrO_2 decreases the total acidity from to 53% its original value with 15% Ni and to 86% for 30% Ni.

Pt addition in the case of the 1.0Pt/SZ catalyst produced a minor increase of the total acidity. Regarding the acid distribution it can can be seen that Ni/SZ

Table 1
Amount of acid (total, Brönsted and Lewis) and strength distribution as measured by TPD of pyridine (Py)

Catalysts	Total Acidity [μmol Py g^{-1}]	Acidity distribution [μmol Py g^{-1}]		
		Weak (150–300 °C)	Medium (300–500 °C)	Strong (500–650 °C)
SZ	238	57.2	83.4	97.0
0.1Ni/SZ	44.4	1.4	24.6	18.4
0.5Ni/SZ	147	52.4	76.8	17.8
1.0Ni/SZ	188	118	52.0	17.0
5.0Ni/SZ	218	129	75.0	14.0
1.0Pt/SZ	280	56	184	106

Table 2
Initial hydroconversion of *n*-octane (at 5 min time-on-stream)

Sample	Conv. (%)	S_{nP} (%)	S_{iP} (%)	Selectivity (%) and yield (%)					
				C_1–C_3	i-C_4	i-C_{5-7}	i-C_8	$C_{4-8=}$	Y_{iP}
SZ	87.0	41.7	56.1	13.6	39.7	13.8	2.7	0.0	48.7
0.1Ni/SZ	52.6	25.9	73.0	15.4	54.3	17.1	1.5	0.4	38.0
0.5Ni/SZ	69.3	27.9	71.3	16.6	54.2	16.2	0.9	0.3	49.4
1.0Ni/SZ	70.7	28.6	70.7	16.9	54.1	15.8	0.8	0.2	50.0
5.0Ni/SZ	72.5	30.0	69.4	17.1	53.5	15.2	0.7	0.2	48.8
0.1Pt/SZ	89.5	45.9	53.2	17.6	36.6	16.2	0.4	0.0	47.6
0.5Pt/SZ	98.7	48.7	50.7	18.1	34.0	16.6	0.1	0.0	50.1
1.0Pt/SZ	99.9	50.8	48.4	18.6	33.8	14.7	0.0	0.0	48.3

mainly has sites of weak and medium strength while SZ and Pt/SZ have mainly sites of medium and high strength.

Figure 2 shows the evolution of the conversion during the reaction of *n*-octane. The results of 0.5–1.0% were practically identical so only one series was plotted. The SZ catalyst suffers great deactivation during the first hour of reaction. Pt addition greatly improves the stability. Ni addition has only a minor effect. Fast deactivation is produced by the blocking of the acid active sites by coke.

At 5 min time-on-stream the activity drop is not so acute and a comparison can be made between the different catalysts. Table 1 contains both conversion and selectivity values. The selectivity to shorter paraffins indicates the presence of hydrocracking while the selectivity to short and long isoparaffins indicates the presence of hydroisomerization. The initial activity of SZ is high and is increased even more by Pt addition. Increasing Pt contents improve both the stability and the initial conversion. The selectivity to isoparaffins is only slightly decreased by Pt addition. The major effects of Pt addition are the increase of the stability and of the hydrogenating capacity. Both effects are sensitive to the Pt content and are enhanced at higher percentages of the noble metal. Conversely Ni addition mostly negatively affects the activity of SZ. A small amount of Ni (0.1%) produces a drop in conversion from 87% to 52%. Increasing Ni amounts are able to recover part of the lost conversion level. A 1% Ni catalyst has a 71% conversion. The presence of Ni has also a moderate effect on the stability, that is slightly improved. Though Ni is not mainly present as metallic Ni, it seemingly can produce a small amount of activated hydrogen which is able to partially hydrogenate coke precursors. Ni clearly has less capacity than Pt to activate hydrogen but its addition improves the selectivity towards isoparaffins and decreases the yield to deep cracking products (C_1–C_3).

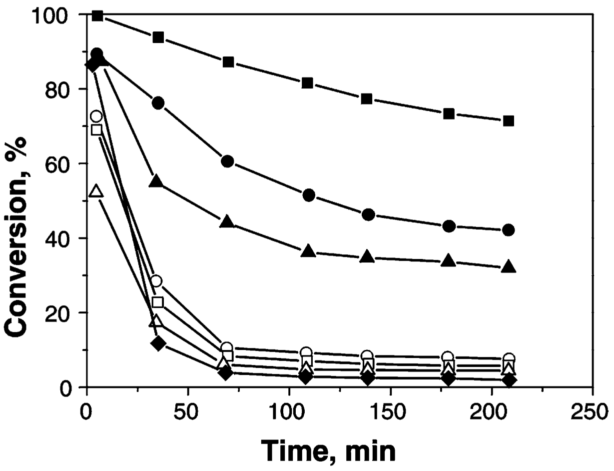

Figure 2. *n*-Octane hydroconversion as a function of time-on-stream. (■) 1.0Pt/SZ. (●) 0.5Pt/SZ. (▲) 0.1Pt/SZ. (◆) SZ. (○) 1.0Ni/SZ. (□) 0.5Ni/SZ. (δ) 0.1Ni/SZ.

The main cracking products are C_3, i-C_4, *n*-C_4 and i-C_5. i-C_4 is always the most important cracking product. S_{nP} is the selectivity to normal paraffins produced by cracking and S_{iP} is the selectivity to isoparaffins obtained by isomerization (i-C_8) and by isomerization-cracking (i-C_4– i-C_7). In the case of the Ni catalysts the increase of S_{iP} is not due to an increase in the i-C_8 yield but to a greater i-C_4 production. The iso/normal ratio of the C_4, $C_{5–7}$ ant total paraffins is higher for the Ni-promoted catalysts. An optimum Ni content of 1% maximizes the iso/normal ratio.

The isoparaffin yield (Y_{ip}) of the 0.5–1.0% Ni-promoted catalysts is similar to those of SZ and Pt/SZ. Though Pt enhances the activity of SZ, it also decreases the selectivity to isoparaffins. In the balance, Y_{iP} is not altered. The good yield of isoparaffins at small conversion values in the case of Ni could enable an improved production of isoparaffins by using a scheme of recycle.

Table 3 contains data on the performance of different catalysts in reactions of hydroisomerization-cracking of long paraffins. An inspection of these data indicates that

Table 3
Comparison of current and previously reported results on the isomerization-cracking of long-chain alkanes

Catalysts	Feed	T (°C)	P_{HC} (kPa)	P_{H2} (Mpa)	W/F_{HC} (g h mol^{-1})	TOS (h)	Conv. (%)	Selec. iso (%)	Ref.
Pt(0.5%)/HY	*n*-C_9	270	30	0.45	36	n.a.	82.0	n.a.	[24]
Pt(0.5%)/HZSM-5	*n*-C_{10}	270	20	2.0	130	n.a.	98.2	25.6	[25]
Pt(0.5%)/HZSM-5	*n*-C_9	280	20	2.0	130	n.a	98.5	18.9	[25]
Pt(1.0%)/HZSM-22	*n*-C_{10}	180–280	700	1.8	68	> 1	80.0	78.7	[26]
Pt(1.5%)/HY	*n*-C_{10}	200	11	0.1	< 400	n.a.	70.0	66.6	[27]
Pt(0.35%)/HY	*n*-C_{10}	200	11	0.1	< 400	n.a.	60.0	62.5	[27]
Pt(0.5%)/WZ	*n*-C_{16}	300	700	1.4	75	6	95.0	37.0	[28]
Pt(0.3%)/H-MOR	*n*-C_8	300	210	1.3	60	5	67.9	24.2	[29]
Ni(0.5%)/SZ	*n*-C_8	300	50	1.5	28.5	0.1	69.3	71.3	this work

TOS = Time-on-stream; n.a. = not available.

The values of activity and selectivity taken from the articles were chosen for conditions of maximum yield of isomers. Where more than one result was available the experiment with the W/F value closest to ours was chosen.

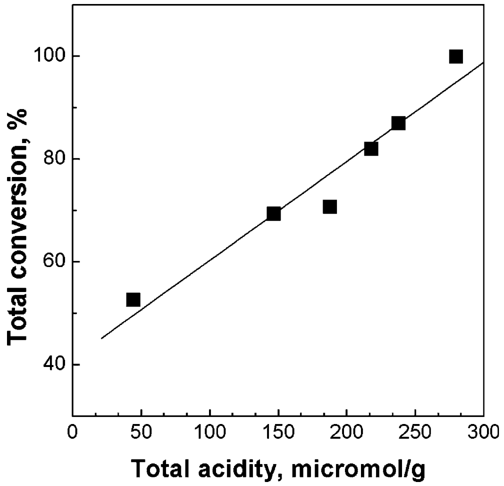

Figure 3. Total conversion of *n*-octane at 5 min time-on-stream, as a function of the total acidity (SZ, 1.0Pt/SZ and Ni/SZ samples).

Ni/SZ catalysts are among the most selective catalysts. As any member of the SZ family and as depicted in figure 2, Ni/SZ suffer from deactivation by coking. Most coking would be associated to the fast deactivation of strong acid sites during the first stage of the reaction [30]. Coke deposits of about 1% carbon would be formed and slow coking would continue until a regeneration step is needed in which the coke deposits are eliminated. Coke elimination can procceed by oxidation at 500 °C [30] or by hydrogenation [31].

Figure 3 is a plot of the conversion at 5 min of time-on-stream as a function of total acidity. It can be seen that the intrinsic activity of the oxoanion promoted catalysts during hydroconversion of long-paraffins is directly related to the amount of surface acid sites. It can then be accepted that the conversion drop due to Ni promotion is due to the dimminution of the amount of acid sites of SZ. According to the results of table 1 this effect is related to blocking of most acid sites at low Ni contents (0.1%) and to blocking of strong acid sites and creation of new ones of weak and medium strength at higher Ni contents.

4. Conclusions

SO_4^{2-}–ZrO_2 is an adequate catalyst for isomerization-cracking of long paraffins because a good yield of C_4–C_6 isoparaffins is obtained at 300 °C. Pt addition does not modify the selectivity but improves the stability. Ni addition decreases the acid activity of the support and increases the selectivity to branched isomers by reducing deep cracking. The stability of the Ni promoted SO_4^{2-}–ZrO_2 catalysts is much lower than that of the Pt promoted ones. The reason is that Ni is not in the metal state in Ni/SO_4^{2-}–ZrO_2 and it has a much lower capacity to produce activated hydrogen.

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