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NOTE

SO_4^{2-}–ZrO_2 and Pt/SO_4^{2-}–ZrO_2: Activity and Stability during *n*-Hexane Isomerization

Sulfate promoted zirconia (SZ) is a well-known alkane isomerization catalyst (1, 2). Most of the studies related to this catalyst have been carried out taking the isomerization of *n*-butane and *n*-pentane as the test reaction. Garín *et al.* (3), working under a hydrogen partial pressure of 8×10^{-2} kg cm^{-2} and 1.033 kg cm^{-2} total pressure, studied the effect of platinum on *n*-butane isomerization and observed that platinum gives stability to the catalyst. Ebitani *et al.* (4) did not observe *n*-pentane isomerization activity on Pt(0.5%)/SO_4^{2-}–ZrO_2 (PtSZ) at 523 K and atmospheric pressure (34×10^{-2} kg cm^{-2} *n*-pentane partial pressure) using nitrogen as carrier gas, while the activity appeared when nitrogen was changed by hydrogen. They considered that molecular hydrogen is homolitically dissociated on platinum; the H atoms migrate by spillover to the SZ, where they are transformed into H^+ and an electron or to H^- on a Lewis acid site. The H^+ displays a catalytic role in the skeletal *n*-pentane isomerization, while stability is obtained due to the presence of H^- which weakens the strong Lewis sites, responsible for coke formation. Iglesia *et al.* (5) suggested that the *n*-alkanes activation is produced through a chain transfer mechanism in which the limiting step is the hydride transfer which allows the replacement of the carbenium ions present on the acid sites. They considered that molecular hydrogen, through a heterolytic dissociation over the metal, is a hydride source. Hosoi *et al.* (6) considered that SZ deactivation during *n*-pentane isomerization in the presence of hydrogen at 453 K is produced by the formation of coke precursors on the strong acid sites; the addition of a metal like Pt, Pd, or Rh provides catalyst stability. Chen *et al.* (7) arrived at a similar conclusion; from Uv-vis studies they observed the formation of “allylic species” which neutralized the acid sites of SZ, but these species were not observed on Pt(0.2%)SZ in the presence of hydrogen. These authors as well as Garín *et al.* (3) considered that hydrogen (even without platinum) inhibits coke formation due to the hydrogenation of nonsaturated hydrocarbons. Keogh *et al.* (8) found that the loss of activity of PtSZ during *n*-hexadecane isomerization at 423 K is produced due to the deactivation of the acid sites by coke deposition and not because of the deactivation of the metal. Ng and Horvát (9) considered that deactivation of SZ during *n*-butane reaction at 523 K (without hydrogen) is due to the change of sulfur oxidation state, sulfur elimination, and coke formation.

Our objective is to study the role of both platinum and hydrogen on the activity and stability of SZ and PtSZ during *n*-hexane isomerization, analyzing the possible reaction mechanism and the reasons for catalyst deactivation.

$Zr(OH)_4$ was prepared as previously described (10). The platinum was added (previous to sulfate) impregnating the zirconium hydroxide by the incipient wetness technique using a $H_2PtCl_6 \cdot 6H_2O$ solution with the adequate concentration to obtain 0.5% platinum on the solid. This material was dried at 383 K for 12 h. Sulfate was added by dipping the dried zirconium hydroxide, with or without platinum, in a 0.5 M sulfuric acid solution (concentration previously reported as the optimum one (2)) for 1 h without stirring and with 2.2 ml g^{-1} acid solution/solid ratio. These sulfated samples were filtered and dried at 383 K for 12 h.

Platinum concentration was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Perkin-Elmer ICP/5500 plasma spectrometer and sulfur by combustion in a LECO CS-244 analyzer.

Catalytic activity and selectivity for the *n*-hexane isomerization reaction were measured in a flow fixed-bed tubular reactor; 1 g of catalyst sieved to 35–80 mesh was charged for the test. Catalysts were calcined 3 h at 873 K in an air stream and cooled overnight to room temperature in a nitrogen flow. The reaction was performed by feeding *n*-hexane (Merck p.a.) during 9 or 360 min at 473 K, 6 kg cm^{-2}, 4 h^{-1} weight hourly space velocity, and hydrogen/*n*-hexane or nitrogen/*n*-hexane molar ratio of 6. Special attention was given to the first minutes on stream, collecting product samples in a 16-port multiloop sampling valve. *n*-Hexane and reaction products were analyzed by on-line gas chromatography using a 100-m-long column packed with squalene.

TPO analysis of used catalysts were performed in a specially designed equipment (11) in order to improve both sensitivity and resolution due to the low coke content of some samples. The unit converted the CO_2 generated during coke combustion to CH_4, using a Ni catalyst. The CH_4 was then analyzed with a flame ionization detector. The experiments were performed using a 6% O_2/N_2 (20 ml min^{-1}) stream, heating at 12 K min^{-1}. Sample weight was 0.04 g. The H/C ratio was determined measuring the CO_2

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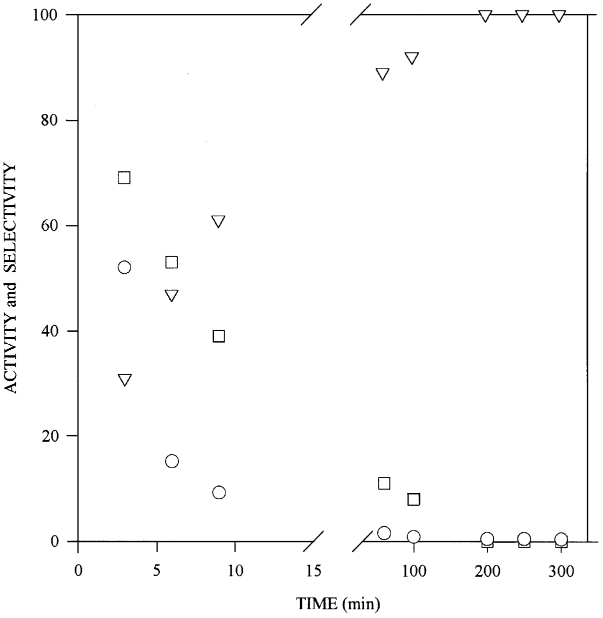

FIG. 1. Activity [moles of *n*-hexane converted × (mole of sulfur)$^{-1}$ × h^{-1}] (◯), and selectivity (%) to cracking (☐) and to C_6 products (▽) for PtSZ run with N_2. $T = 473$ K; $P = 6$ kg cm^{-2}; WHSV = 4 h^{-1} and N_2/*n*-hexane molar ratio = 6.

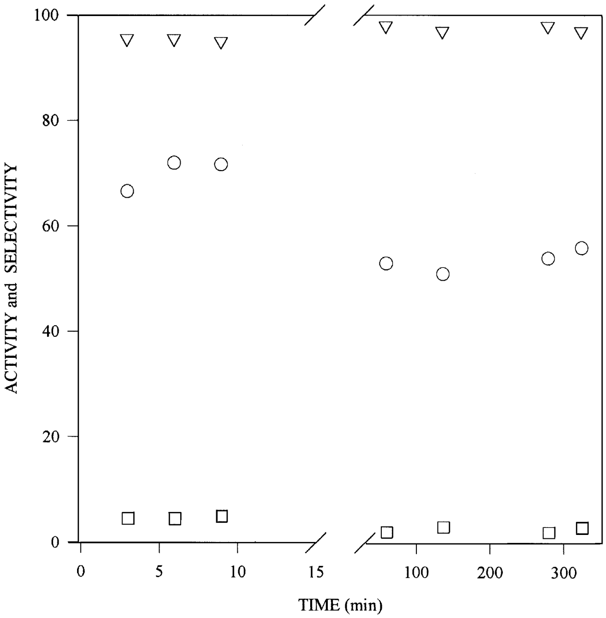

FIG. 2. Activity [moles of *n*-hexane converted × (mole of sulfur)$^{-1}$ × h^{-1}] (◯), and selectivity (%) to cracking (☐) and to C_6 products (▽) for PtSZ run with H_2. $T = 473$ K; $P = 6$ kg cm^{-2}; WHSV = 4 h^{-1} and H_2/*n*-hexane molar ratio = 6.

produced and the O_2 consumed when coke is burned using a 1% O_2/He stream and the same heating rate as in TPO analysis; more details of the technique have been previously reported (12).

SZ run either with N_2 (SZN_2) or H_2 (SZH_2) and Pt(0.56%)SZ run with N_2 ($PtSZN_2$), show a similar behavior during *n*-hexane reaction (see Fig. 1 for $PtSZN_2$ as an example). At short time-on-stream (3 min) *n*-hexane activity is about 52 moles of *n*-hexane converted × (mole of sulfur)$^{-1}$ × h^{-1}, mainly to cracking products; a low isomerization activity appears with time. The behavior is different for PtSZ run with H_2 ($PtSZH_2$), as shown in Fig. 2; a higher *n*-hexane activity than in the former case and a good stability are observed. There is a high *n*-hexane selectivity to isomers, being low the selectivity to cracking products. The composition of the C_6 fraction for both catalysts, run either with N_2 or H_2 at different times-on-stream, is shown in Table 1. SZN_2, SZH_2, and $PtSZN_2$ show a decrease in 2-methylpentane (2MP) which corresponds to an increase of methylcyclopentane (MCP) with time-on-stream, the increment in MCP being more noticeable for $PtSZN_2$; 2,2-DMB also decreases with time. The product distribution remains practically constant with time-on-stream for $PtSZH_2$. The light fraction includes only C_3–C_5, mainly C_4, as it is presented in Table 2 for 6 min time-on-stream; almost the same distribution is obtained for longer times-on-stream.

The sulfur content of the fresh catalysts and after being run either under hydrogen or nitrogen atmospheres during either 9 or 360 min, and the carbon content of used catalysts, are presented in Table 3. There exists an important loss of sulfur during the run, being the decrease higher for the SZ samples than for the PtSZ ones. The largest loss is produced on SZN_2, in the absence of both platinum and hydrogen. Sulfur is present mainly as S^{6+} species on SZ and PtSZ surfaces (10, 13). The reduction of S^{6+} species in the presence of hydrogen and platinum is not expected at the reaction temperature, 473 K (6, 13). Then, the sulfur loss might be

TABLE 1

Product Distribution in the C_6 Fraction for SZ and PtSZ Run with N_2 or H_2 for Different Times-on-Stream

Catalyst	Time (min)	$X_{n\text{-}C_6}$ (%)	2MP (%)	3MP (%)	23DMB (%)	22DMB (%)	MCP (%)	CH (%)
SZN_2	6	18	51.8	29.9	14.8	3.5	0	0
	9	9	50.9	29.7	14.7	1.9	0	2.8
	320	0.5	44.8	30.1	10.8	0	11.2	3.1
SZH_2	6	19	51.8	29.3	14.2	3.4	0.4	0.9
	9	10	52.2	29.3	14.2	2.8	1.2	0.3
	320	0.6	45.6	30.0	10.0	0.9	10.5	3.0
$PtSZN_2$	6	18	53.8	29.1	12.6	2.6	0.5	1.4
	9	9	54.1	29.1	12.7	1.8	0.9	1.4
	320	0.5	10.1	40.1	0	0	49.8	0
$PtSZH_2$	6	81	46.7	27.9	12.2	13.1	0.1	0
	9	79	47.2	28.7	11.8	12.3	0	0
	320	54	47.0	29.0	12.0	12.0	0	0

Note. $X_{n\text{-}C_6}$ = *n*-hexane conversion.

TABLE 2

C_1–C_5 Percentual Product Distribution at 6 min Time-on-Stream

Catalyst	$X_{n\text{-}C_6}$ (%)	Distribution (%)				
		C_1	C_2	C_3	C_4	C_5
SZN_2	18	0	0	29.5	58.6	11.9
SZH_2	19	0	0	22.3	57.4	20.3
$PtSZN_2$	18	0	0	23.9	60.9	15.2
$PtSZH_2$	81	0	0	21.1	56.5	22.4

Note. $X_{n\text{-}C_6} = n$-hexane conversion.

related to the isomerization process itself, as proposed by Ng and Horvát (9) working at atmospheric pressure and 523 K in *n*-butane isomerization. Our results are different from those of Keogh *et al.* (8), who observed a negligible sulfur loss during *n*-hexadecane isomerization at 7.8 kg cm^{-2} hydrogen pressure and 423 K on Pt(0.6%)/SO_4^{2-}–ZrO_2 in the presence of hydrogen.

Regarding coke deposition on SZ, it can be seen that there are no important differences between the samples used in nitrogen or hydrogen during 9 or 360 min. For $PtSZN_2$ and $PtSZH_2$, a larger amount of coke is observed after 360 min. When both platinum and hydrogen are present, the amount of coke is small at short times-on-stream, but is large at longer times, when compared with SZH_2 or SZN_2.

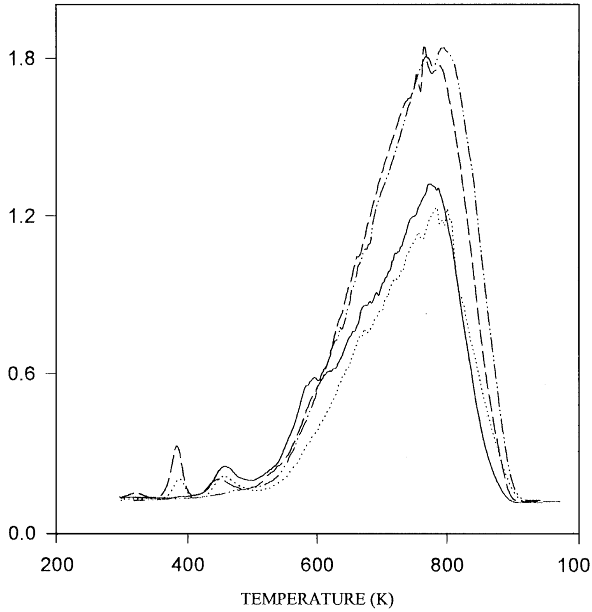

FIG. 3. Thermal-programmed-oxidation of several SZ samples: ——— SZH_2 run during 9 min; .... SZN_2 run during 9 min; _._._._ SZH_2 run during 360 min; _ _ _ _ _ SZN_2 run during 360 min.

Figure 3 shows the TPO profiles of SZN_2 and SZH_2 run during 9 and 360 min. A similar pattern is observed for all of them, the maximum of the main peak being at about 790 K, with a logical increase of the area under the curves for longer times-on-stream. Figure 4 shows TPO profiles for PtSZ samples. The profile corresponding to $PtSZN_2$ run during 360 min, although larger, is similar to those presented in Fig. 3, but with a shoulder at about 600 K. Nevertheless, when both platinum and hydrogen are present, the profile is different: a broad peak with the maximum at 620 K and a sharp peak centered at about 460 K, the last probably being related to coke over platinum, are observed. These different TPO profiles cannot be attributed to a catalytic action of platinum on coke burning, because platinum is present in both cases. Both profiles may indicate distinct burning kinetics associated with coke of different nature. The H/C ratio for $PtSZH_2$ and $PtSZN_2$ (runned during 360 min) are 0.80 and 0.65, respectively, indicating that the coke for the former sample is more hydrogenated and less polymerized than the coke on $PtSZN_2$. SZ and PtSZ run with N_2 show a peak with maximum at about 373 K that can be attributed to adsorbed hydrocarbons which desorbed during heating and are transformed into methane on the nickel catalyst.

A very different selectivity has been observed for SZN_2, SZH_2, and $PtSZN_2$ when compared with $PtSZH_2$ (see Figs. 1 and 2). For the former ones, the main products are cracking ones in the C_3–C_5 range and catalysts are rapidly deactivated. For $PtSZH_2$ the main products are C_6 isomers and the catalyst presents a good stability. From these results it can be inferred that both platinum and hydrogen participate in the *n*-hexane isomerization mechanism. The following reaction scheme can be proposed: a carbenium ion is formed and isomerized on an acid site; for SZH_2, SZN_2, or $PtSZN_2$, the carbenium ion is transformed into coke and cracking products, the latter ones through a direct mid-molecule β-scission of a bi or trimolecular intermediate (5), because the cracking products are C_3–C_5 hydrocarbons, mainly C_4.

TABLE 3

Sulfur Content of Fresh and Used Catalysts and Carbon Content of Used Catalysts, Run during 9 or 360 min

Catalyst	SZ[a]	SZN_2	SZN_2	SZH_2	SZH_2	PtSZ[a]	$PtSZN_2$	$PtSZN_2$	$PtSZH_2$	$PtSZH_2$
Time (min)	0	9	360	9	360	0	9	360	9	360
S (wt%)	2.2	1.4	1.0	1.4	1.3	1.8	1.6	1.5	1.6	1.3
C (wt%)	0	0.17	0.25	0.19	0.27	0	0.14	1.23	0.04	0.92

[a] Fresh catalyst.

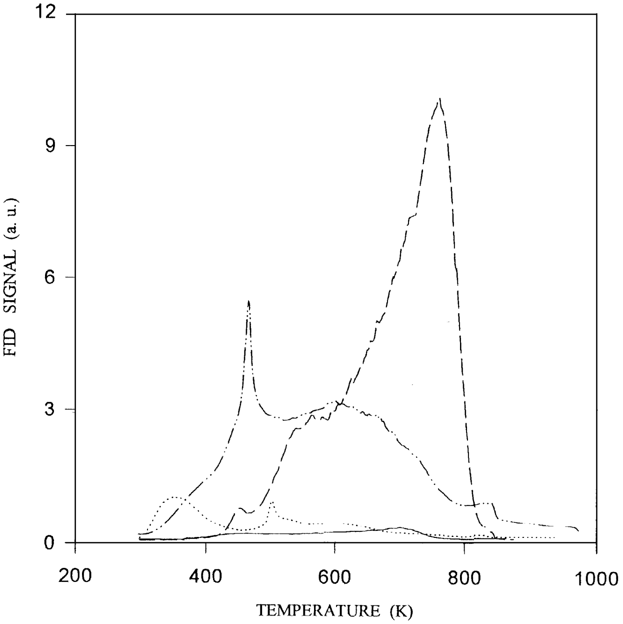

FIG. 4. Thermal-programmed-oxidation of several PtSZ samples: ——— $PtSZH_2$ run during 9 min; .... $PtSZN_2$ run during 9 min; _.._.._ $PtSZH_2$ run during 360 min; _ _ _ _ _ $PtSZN_2$ run during 360 min.

For $PtSZH_2$, when both platinum and hydrogen are present, the high isomerization selectivity can be explained considering that platinum heterolytically dissociates hydrogen, generating hydrides, as proposed by Iglesia *et al.* (5). The hydride interacts the isomerized carbenium ion, giving the isomeric hexane; this is the limiting step in the reaction mechanism. More carbenium ions are formed from *n*-hexane and they are isomerized on the acid sites. When hydrides are not present, because of the absence of platinum or hydrogen, the carbenium ions remain long time at the surface, they are either oligomerized and then cracked or polymerized into coke. The former considerations are supported by the fact that a positive effect of total and hydrogen partial pressure was observed in both activity and selectivity to isomers. Cracking is minimum on $PtSZH_2$, but the cracking products are also C_3–C_5 (Table 2), indicating that the mechanism of their formation is also through a bi or trimolecular intermediate. There are controversies about the state of platinum of PtSZ but it is generally accepted that it is in the metallic state (14, 15), although it does not show typical metallic properties like CO chemisorption (13). The situation was explained by considering that platinum is covered by sulfur species (5, 16) but it can still dissociate hydrogen (4).

The rapid deactivation observed on SZN_2, SZH_2, and $PtSZN_2$ cannot be attributed to the loss of sulfur. For example, $PtSZN_2$ has lost 0.2% sulfur after 9 min-on-stream and its activity has decreased; after the same time-on-stream, $PtSZH_2$ has lost a similar amount of sulfur and its activity is the same as the initial one.

There exist differences in coke deposition at 9 min-on-stream between SZN_2, SZH_2, and $PtSZN_2$ when compared to $PtSZH_2$; the amount of coke in the latter catalyst is 4–6 times lower. In the absence of either platinum or hydrogen there is no formation of hydrides and the surface renovation of isomerized carbenium ions is slow. Consequently, this carbenium ions could either oligomerize and crack or polymerize to coke, which deactivates the acid sites. The isomerization activity observed in Fig. 1 would indicate that this reaction is disfavored with respect to cracking and polymerization due to the absence of hydrides; another possibility is that isomerization occurs on weaker acid sites than those required for cracking, which are more rapidly deactivated.

The carbon content of SZ samples is about 0.18% at 9 min-on-stream. Although the acid sites are almost completely deactivated after that time (Fig. 1) the increase in coke at 360 min can be related to the residual activity. The coke deposition, after 360 min-on-stream is higher for the platinum containing samples, which can be explained by considering the dehydrogenating capacity of platinum, as it has also been found comparing Al_2O_3 and Pt/Al_2O_3 (17). The amount of coke is even higher for $PtSZN_2$ run during 360 min, which can be related to the large amount of MCP among the reaction products. MCP is recognized as the greatest coke precursor for metal-acid catalysts (18, 19) among the C_6 hydrocarbons. The larger carbon content on $PtSZN_2$ than the one corresponding to SZ samples can be explained by considering that coke precursors produced on platinum go to weaker acid sites where they can polymerize, while the stronger acid sites responsible for cracking (20) were rapidly deactivated. The TPO profiles show a similar type of coke for SZH_2, SZN_2, and $PtSZN_2$, although the last one presents a shoulder at about 600 K which can be ascribed to the catalytic action of platinum on coke burning (21).

Keogh *et al.* (8) considered that the deactivation of $PtSZH_2$ during *n*-hexadecane isomerization is produced by coke deposition on the strong acid sites. Garín *et al.* (3) have observed that hydrogen prevents coke formation even in the absence of platinum, but their results were obtained using a higher hydrogen/hydrocarbon ratio than the one used in our work. According to our results, $PtSZH_2$ keeps the isomerization activity after 360 min-on-stream despite having 0.92% carbon. Other catalysts are practically inactive at the same time, although having lower amounts of carbon (for example, SZH_2 has 0.27%). The sharp peak at about 450 K in the TPO profile of $PtSZH_2$ run during 360 min, can be ascribed to the combusion of coke on platinum, as it was previously demonstrated for Pt/Al_3O_2 during hydrocarbons reaction (22). We have also observed, from the TPO profile, that coke on $PtSZH_2$ is less polymerized, indicating that hydrides generated on platinum control the polymerization process; this coke has a lower deactivating effect than that on SZN_2, SZH_2, or $PtSZN_2$.

The deactivation observed on PtSZH_2 could not be ascribed to a loss of sulfur; a decrease without a modification in the isomerization activity was observed during the first min-on-stream.

It can be concluded that the high *n*-hexane isomerization activity and stability observed on PtSZH_2 is due to the presence of both hydrogen and platinum. In the absence of one of them, mainly cracking products and a rapid deactivation were observed. Coke produces catalyst deactivation. A less polymerized coke, with a lower deactivation capacity, is formed on PtSZH_2.

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