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Isomerization of *n*-butane on Pt/SO_4^{2-}–ZrO_2 and Mechanical Mixtures of Pt/Al_2O_3 + SO_4^{2-}–ZrO_2

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The effect of the incorporation of a metallic phase (Pt) into a superacid catalyst (SO_4^{2-}–ZrO_2) for *n*-butane isomerization was studied. The convenience of supporting Pt directly on the superacid or on alumina and of using the physical mixture as a catalyst was also analyzed. Pt supported on SO_4^{2-}–ZrO_2 has the same activity as SO_4^{2-}–ZrO_2, but the stability is increased. The bifunctional reaction mechanism is not operating because Pt does not have metallic properties due to a strong interaction with the support under the experimental conditions of reduction (573 K). When Pt is supported on Al_2O_3 and mixed mechanically with SO_4^{2-}–ZrO_2, the activity and stability are increased due to the operation of the bifunctional mechanism.

INTRODUCTION

In a global economic context of reformulation of fuels for the protection of the environment, the production of MTBE and alkylates as substitutes for lead additives and aromatic hydrocarbons in gasolines is getting a sustained boost. Isobutene is the main raw material for the production of both substitutes and it is obtained from refinery gases. Since this source of isobutene is becoming scarce, other sources, such as *n*-butane (*n*-C_4), could be used. In this case, the first step is the isomerization of *n*-butane followed by dehydrogenation. Skeletal isomerization of paraffins can only be performed on strong acid catalysts. The addition of SO_4^{2-} ion to zirconia produces a noticeable increase in its acid strength ($Ho \leq -16$) (1). This enhanced acidity enables SO_4^{2-}/ZrO_2 to catalyze skeletal isomerization of *n*-butane, but fast deactivation of the catalyst appears to be a drawback of its use (2, 3). When the reaction is carried out in the presence of hydrogen, the addition of a metallic phase to SO_4^{2-}–ZrO_2, e.g., Pt, will theoretically enable (a) the reaction to take place via a bifunctional mechanism, a chemical path with less stringent acid strength requirements, and (b) activated hydrogen to be produced over the metal, a species known to inhibit the formation of coke precursors, which in turn deactivate of the catalyst.

Hosoi and co-workers (4) studied the activity of supported Pt on SO_4^{2-}–ZrO_2 in the isomerization of light feeds of C_5–C_6 and found that the isomerizing activity of SO_4^{2-}–ZrO_2 is greatly increased by the addition of a minor amount of Pt. Similar results have been found by Ebitani *et al.* (5) during the isomerization of *n*-C_5. Garin *et al.* (6) postulate that the addition of Pt to SO_4^{2-}–ZrO_2 has no influence on the activity and stability of the catalyst in the isomerization reaction of *n*-C_4 when H_2 is used as a carrier gas at a convenient partial pressure. As can be seen, the role of Pt in Pt/SO_4^{2-}–ZrO_2 and that of H_2 are not clear.

In this work, the convenience of the addition of Pt to SO_4^{2-}–ZrO_2 is reconsidered; catalysts of both the supported (Pt/SO_4^{2-}–ZrO_2) and hybrid mixed types are prepared. In the last case, Pt/Al_2O_3 is used as co-catalyst in a mixture with SO_4^{2-}–ZrO_2.

EXPERIMENTAL

Catalysts

(a) The first step in the preparation of SO_4^{2-}–ZrO_2 was the precipitation of $Zr(OH)_4$ by the hydrolysis of zirconium oxychloride ($ZrOCl_2 \cdot 8\ H_2O$) in an aqueous solution of ammonium hydroxide. A solution of 1 *N* H_2SO_4 was percolated through the dried solid, as described in (3), and then the SO_4^{2-}–$Zr(OH)_4$ substrate was dried overnight at 383 K. Subsequent calcination at 893 K for 3 h yielded the final catalyst, SO_4^{2-}–ZrO_2.

(b) Pt/SO_4^{2-}–ZrO_2 was obtained by impregnation of the SO_4^{2-}–$Zr(OH)_4$ species with a solution of chloroplatinic acid. The volume used for the impregnation was in a 10% excess over the pore volume. The concentration of Pt in the impregnating solution was adjusted in order to obtain a 0.25% Pt catalyst. The Pt/SO_4^{2-}–$Zr(OH)_4$ was then dried overnight at 383 K and, afterward, calcined in air at 893 K for 3 h.

(c) Pt/Al_2O_3 was prepared following the technique de-

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TABLE 1

Catalyst Properties

Sample	SO_4^{2-} (wt%)	Pt (wt%)	Metallic dispersion (100 H/Pt)	Specific surface area (m^2/g)
SO_4^{2-}–ZrO_2	4.5	0.0	[a]	110
Pt/SO_4^{2-}–ZrO_2	5.0	0.25	[a]	100
Pt/Al_2O_3-Cl	—	0.30	80.0	200

[a] No hydrogen chemisorption was detected.

scribed in (7). The alumina support had a specific surface area of 200 m^2/g. The final catalyst contained 0.3% Pt and 0.69% Cl (weight percentages). After being activated in a hydrogen stream at 773 K for 3 h, it was finally stored in a desiccator.

The properties of the catalytic samples can be seen in Table 1. Sulfate was analyzed by attacking the samples with an acid mixture (HI, HCH_3COO, and NaH_2PO_2) in the absence of oxygen for 2 h at 388 K. The H_2S produced was collected in a NaOH solution and titrated with Hg acetate. Pt concentration was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Perkin–Elmer ICP/500 plasma spectrometer.

(d) The mechanical mixtures were prepared by mixing fixed amounts of SO_4^{2-}–$Zr(OH)_4$ with corresponding growing shares of Pt/Al_2O_3. Both substrates had been previously sieved to 35–80 mesh. These mechanical mixtures had to be activated before each run by a 3-h calcination in air at 893 K. The composition of these mechanical mixtures can be seen in Table 2 (samples A-1 to G-1). The ratio of the mass of Pt/Al_2O_3 to the mass of SO_4^{2-}–ZrO_2 was calculated after calcination at 893 K.

TABLE 2

Mechanical Mixtures of Pt/Al_2O_3 and SO_4^{2-}–ZrO_2

Catalyst	Pt/Al_2O_3 to SO_4^{2-}–ZrO_2 Mass ratio	Pt content (wt%) In mixture	Pt content (wt%) Referred to SO_4^{2-}–ZrO_2
A-1	0.0	0.000	0.000
B-1	0.1	0.027	0.030
C-1	0.2	0.050	0.060
D-1	0.4	0.090	0.120
E-1	0.6	0.110	0.180
F-1	0.8	0.130	0.240
G-1	1.0	0.150	0.300
H-2	0.2	0.050	0.060
I-2	0.4	0.090	0.120
J-2	0.6	0.110	0.180
K-2	1.0	0.150	0.300

A variation of the technique outlined above was also carried out. SO_4^{2-}–$Zr(OH)_4$ was first calcined at 893 K for 3 h and then mixed with Pt/Al_2O_3 in an open vessel. These samples were prepared with equal amounts of SO_4^{2-}–$Zr(OH)_4$ and increasing amounts of Pt/Al_2O_3. The composition of samples can be seen in Table 2 (H-2 to K-2).

Materials

The zirconium oxychloride was Merck pro-analysis. H_2SO_4 and NH_4OH were Carlo Erba RPE. The gases were Matheson normal butane (99.5%), pure air, and H_2 provided by AGA.

Hydrogen Adsorption and Specific Surface Area

Hydrogen adsorption isotherms were determined to calculate the dispersion of metallic Pt. Samples were evacuated while being heated from room temperature to 573 K, and were kept for 2 h at this temperature. Then, at the room temperature, several cycles of evacuation and hydrogen pressurization were performed, and finally the isotherms of total and reversible hydrogen adsorption were measured at room temperature. The amount of chemisorbed hydrogen was obtained by subtracting the two isotherms and the metal dispersion was calculated assuming dissociative adsorption of hydrogen on the Pt atoms. For the specific surface area, the catalyst samples were degassed at 573 K for 2 h, and then the nitrogen adsorption isotherm was determined at the temperature of liquid nitrogen. A Micromeritics 2100E apparatus was used for both determinations.

Catalytic Test

The reaction of n-C_4 isomerization was performed at atmospheric pressure using a fixed bed quartz reactor operating under isothermal conditions. It was heated by a controlled-temperature electrical oven. The reactor outlet passed through a sampling valve connected to a gas chromatograph. The 3-h calcination at 893 K quoted above for each catalyst was performed in the reactor previous to each run, except for Pt/SO_4^{2-}–ZrO_2, which was calcined before mixing with Pt/Al_2O_3. Then, the samples were pretreated in a H_2 stream at 573 K for 1 h and tested for catalytic activity. The conditions of the catalytic test included temperature of 573 K, n-C_4 WHSV of 4 h^{-1} (in the case of mixtures, this refers to SO_4^{2-}–ZrO_2), and several different molar H_2/n-C_4 ratios.

The reaction products were analyzed using an on-line gas chromatograph with a FID detector and a 6-m long, $\frac{1}{8}$-in. diameter column packed with 25% dimethylsulfolane on Chromosorb P. From the analysis, the activity and selectivity of each product were calculated.

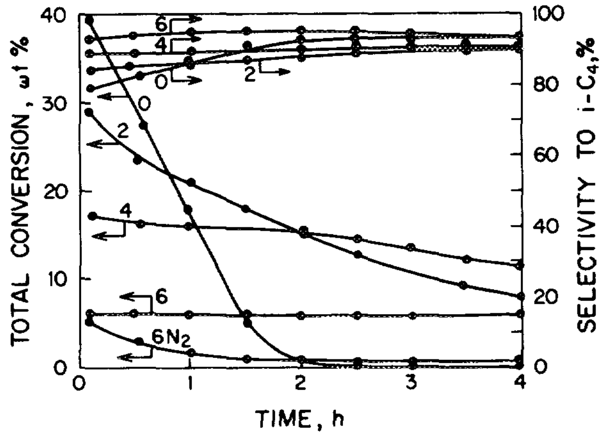

FIG. 1. Total conversion of n-C_4 and selectivity to i-C_4 as a function of time-on-stream. Catalyst: Pt/SO_4^{2-}-ZrO_2, WHSV = 4 h^{-1}, H_2/n-C_4 variable, $T = 573$ K. Numbers over curves mean H_2/n-C_4 molar ratios. 6 N_2 means nitrogen instead of hydrogen: N_2/n-C_4 = 6.

RESULTS AND DISCUSSION

a. Pt/SO_4^{2-}-ZrO_2 and SO_4^{2-}-ZrO_2

Values of total conversion of n-C_4 and selectivity to i-C_4 on Pt/SO_4^{2-}-ZrO_2 are plotted in Fig. 1 as a function of time. A WHSV value of 4 h^{-1} and several H_2/n-C_4 molar ratios (0, 2, 4, and 6) were used in order to analyze the effect of hydrogen. The first four lines of Table 3 show the initial values (at 5 min time on stream) of n-C_4 conversion and of the selectivities to reaction products as a function of the H_2/n-C_4 ratio. For pure n-butane (H_2/n-C_4 ratio = 0), a fast deactivation of the catalyst was observed: the initial conversion was high, but after 2 h of time on stream the catalyst was practically deactivated. From Fig. 1 and Table 3 it is possible to conclude that the presence of hydrogen in the feed produces three effects: (a) a diminution in the initial values of conversion due to the decrease in the partial pressure of the hydrocarbon because of the increase in the hydrogen flow rate (another reason for the conversion decrease could be the competition for active sites between n-C_4 and hydrogen, as quoted before (6); (b) a smoothing of the activity drop due to the inhibition of the formation of coke precursors (for a reaction temperature of 573 K, H_2/n-C_4 molar ratios ≥ 6 are needed to have a stable catalyst); and (c) an increase in selectivity values, probably due to a modification of the reaction intermediates diminishing cracking ($C_1 + C_2 + C_3$) and disproportionation ($C_3 + C_5$), or to a decrease in the successive cracking of more reactive i-C4 because of the decrease in conversion. In the absence of hydrogen, the activity drop coincides with an increase in selectivity because of a decrease in successive cracking reactions and because coke is preferentially deposited on the stronger acid sites which are mainly responsible for the cracking and disproportionation reactions.

With pure n-C_4 the conversion at 5 min time on stream was 39.6% (Table 3), which corresponds to a turnover number of 1.5×10^{-2} molecules of n-C_4 reacted per second per SO_4^{2-} group.

Conversion and selectivity values as a function of time are plotted in Fig. 2 for the SO_4^{2-}-ZrO_2 catalyst using different values of WHSV. A H_2/n-C_4 molar ratio of 6 was chosen because Pt/SO_4^{2-}-ZrO_2 is stable at this ratio. Comparing the results of Fig. 2 with the corresponding results for Pt/SO_4^{2-}-ZrO_2 and WHSV = 4 (Fig. 1), it can be seen that (i) the addition of Pt to SO_4^{2-}-ZrO_2 does not modify initial conversion values (at 5 min) and (ii) when no metal is present, the use of a H_2/n-C_4 molar ratio of 6 is not enough to prevent the deactivation of SO_4^{2-}-ZrO_2 at 573 K.

In order to study the influence of hydrogen, several runs in which nitrogen substituted for hydrogen were performed. A run performed with nitrogen is indicated by N_2 in Fig. 1; in this case, the initial activity (5 min) is approximately the same whether the diluent is nitrogen or hy-

TABLE 3

Conversion of n-Butane and Product Selectivities at 5 min Time-on-Stream

Catalyst	WHSV	H_2/n-C_4	Conv.	S_{C1}	S_{C2}	S_{C3}	$S_{i\text{-}C4}$	S_{C5}
Pt/SO_4^{2-}-ZrO_2	4	0	39.6	0.25	1.26	13.13	76.01	9.34
Pt/SO_4^{2-}-ZrO_2	4	2	29.3	—	1.02	8.87	82.6	7.5
Pt/SO_4^{2-}-ZrO_2	4	4	17.4	—	1.15	5.74	87.35	5.75
Pt/SO_4^{2-}-ZrO_2	4	6	6.0	—	1.66	5	95	—
Pt/Al_2O_3	0.36	6	3.0	3.33	20	13.33	53.3	10
Pt/Al_2O_3 + SO_4^{2-}-ZrO_2 (Catalyst G-1)	0.36	6	39.8	0.75	4.27	13.82	73.6	7.28

Note. Conversion and selectivities in mass basis (chromatographic analysis); conv. is the conversion of n-C_4; S_{Ci} is the selectivity to C_i hydrocarbon; C_1 is methane, C_2 is ethane, C_3 is propane, C_5 is (n + i) pentane. Temperature is 573 K and [WHSV] = 1/h.

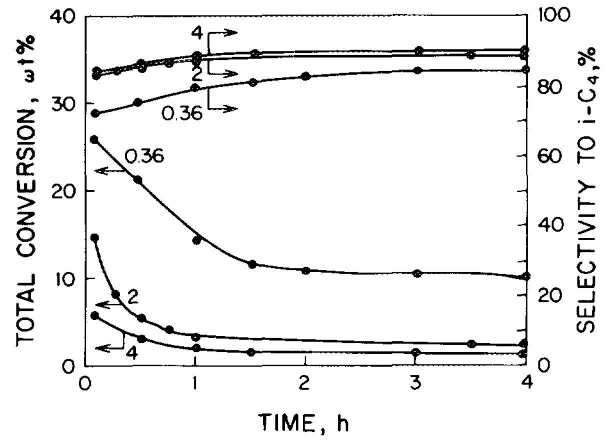

FIG. 2. Total conversion of n-C_4 and selectivity to i-C_4 as a function of time-on-stream. Catalyst: SO_4^{2-}-ZrO_2; T = 573 K; H_2/n-C_4 = 6; WHSV values are indicated on the curves.

drogen but, in the first case, the catalyst deactivates more rapidly.

Initial conversion (5 min) values for SO_4^{2-}-ZrO_2 (with hydrogen) and Pt/SO_4^{2-}-ZrO_2 (with hydrogen or nitrogen) are plotted in Fig. 3. The ratios H_2/n-C_4 and N_2/n-C_4 are both equal to 6. In the case of Pt/SO_4^{2-}-ZrO_2, with a hydrogen-containing feed, the values at 5 min are the same as the ones during the whole run, since no significant deactivation takes place. Similar values of initial activities for the three catalysts can be seen for all values of WHSV used. The addition of the metallic phase produces a beneficial effect on the selectivity when hydrogen is present and when conversions are relatively low. The following conclusions can be stated: (i) The addition of the metallic phase does not produce an increase in the activity of sulfated zirconia, in contrast to what would be expected for the classical bifunctional mechanism of the reaction; thus, the isomerization of n-C_4 could proceed in accord with a monofunctional acid mechanism in both cases, with or without Pt. (ii) The effect of Pt is limited to the generation of activated hydrogen able to inhibit the formation of coke precursors. Seemingly, this activated hydrogen modifies the intermediates of the reaction system, improving the selectivity toward i-C_4. (iii) The hydrogen has little stabilizing effect when there is no Pt present.

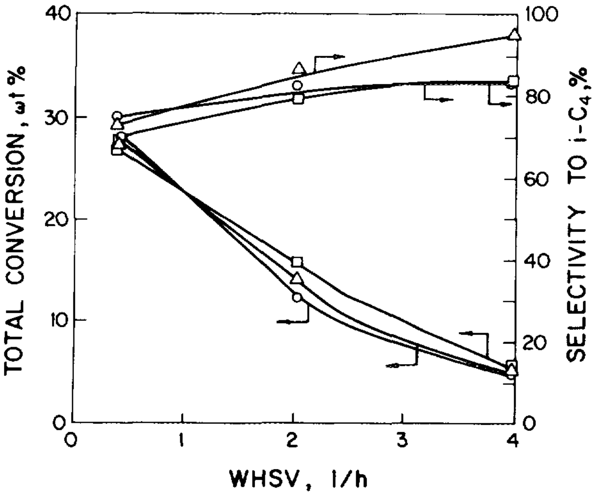

FIG. 3. Total conversion of n-C_4 and selectivity to i-C_4, initial values, at 5 min time-on-stream, as a function of WHSV; (△) Pt/SO_4^{2-}-ZrO_2 with hydrogen; (○) Pt/SO_4^{2-}-ZrO_2 with nitrogen, and (□) SO_4^{2-}-ZrO_2 with hydrogen.

The effect of Pt on Pt/SO_4^{2-}-ZrO_2 is different from that found in Pt/Al_2O_3 and other catalysts where the metal/acid system allows a bifunctional mechanism of isomerization which produces a greater conversion of reactants than the acid monofunctional system. The difference can be assigned to the influence of SO_4^{2-} on the metallic function. Sulfur or SO_4^{2-} can interact electronically with Pt or/and be chemisorbed on the superficial Pt atoms, thus forming a layer which could prevent the access of n-C_4 molecules to the de/hydrogenating metallic sites. There is no agreement in the literature regarding the state of Pt in this catalyst. Ebitani and co-workers (5, 8) compared the hydrogenating activity of Pt/SO_4^{2-}-ZrO_2 and Pt/ZrO_2 by means of the reaction of isomerization of cyclopropane in the presence of deuterium. They found that the presence of SO_4^{2-} suppresses drastically the de/hydrogenating activity of Pt/SO_4^{2-}-ZrO_2 and stated that Pt, when reduced with hydrogen at temperatures below 673 K, is in a cationic state and that part of the metallic particles are covered with sulfur. On the other hand, Paal *et al.* (9) suggest that Pt is mainly in the metallic state but covered with chemisorbed sulfur. Dicko and Sayari (10) support similar conclusions and report that due to sulfur poisoning, Pt does not show typical metallic properties. According to Hattori (11), a large fraction of platinum is in the state of unreduced platinum oxide, a smaller fraction is covered by sulfur, and an even smaller fraction is in the form of metallic platinum. Undoubtedly, whatever the state of Pt in Pt/SO_4^{2-}-ZrO_2, it does not have the catalytic properties of the metallic function. In our experiments, the pretreatment with hydrogen at 573 K is not enough to impart metallic properties to Pt. It is not possible to use higher temperatures because SO_4^{2-} (the cause of catalytic activity) is destroyed. The high concentration (compared with other catalysts) of sulfur as sulfate, sulfide, elemental sulfur, etc., on the support, which is the result of the preparation method, produces a strong interaction of Pt with the support. This interaction must be very strong because the presence of only sulfur is not enough to poison the Pt dehydrogenation activity, as shown by Silvestri *et al.* (13). These authors found that when feeding n-heptane doped with 100 ppm of thiophene it is still possible to produce olefins on Pt and that, in the presence of acid sites, the bifunctional mechanism is possible. Even in our case in which the bifunctional mechanism of reaction is not in operation, the presence of Pt activates hydrogen molecules which can spill over to SO_4^{2-}–ZrO_2 where they suppress the formation of deactivating carbonaceous deposits. In any case, a minimum partial pressure of hydrogen (H_2/n-$C_4 \geq 6$) is necessary in order to generate enough activated hydrogen to suppress deactivation. Pt/SO_4^{2-}–ZrO_2 catalyst is unable to adsorb hydrogen at room temperature, as indicated in Table 1; the adsorption occurs at high temperatures where hydrogen can spill over to the support, according to Tanaka *et al.* (12).

b. Mechanical Mixtures of Pt/Al_2O_3 and SO_4^{2-}–ZrO_2

The catalytic tests with the mecanically mixed catalysts shown in Table 2 were performed at 573 K, with a WHSV of 0.36 h^{-1} and a H_2/n-C_4 molar ratio of 6. In order to examine the influence of the addition of Pt/Al_2O_3, the values of activity and selectivity to *i*-C_4 of some mixtures are plotted in Fig. 4 as a function of time. In the last two lines of Table 3 the conversion and selectivity to the products are shown for Pt/Al_2O_3 and the mixture with a ratio equal to one. The conversion and selectivity to *i*-C_4 for all the mixtures at 4 h on stream are plotted in Fig. 5. It can be seen that the catalytic activity and selectivity of pure Pt/Al_2O_3 are very low and that the addition of Pt/Al_2O_3 gives SO_4^{2-}–ZrO_2 better stability. A mass ratio of 0.4 is enough to prevent the deactivation of the catalyst. Considering the *n*-C_4 conversion at 4 h as the catalytic activity of the samples, it increases with the ratio Pt/Al_2O_3/SO_4^{2-}–ZrO_2 up to a value of 0.4 of the ratio (D-1 catalyst) and remains practically constant for higher mass ratios. The selectivity of *i*-C_4 increases significantly with the initial addition of Pt/Al_2O_3 and then decreases with larger additions due to the influence of the low selectivity of Pt/Al_2O_3, as shown in Table 3. There is an increase in the initial values (at 5 min) of conversion with the addition of Pt/Al_2O_3 and at this time on stream it can be considered that the acid sites are practically "clean."

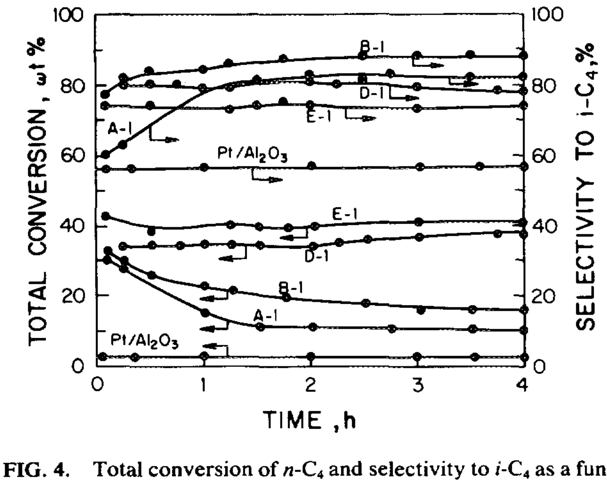

FIG. 4. Total conversion of *n*-C_4 and selectivity to *i*-C_4 as a function of time-on-stream. Catalyst: mechanical mixtures Pt/Al_2O_3 + SO_4^{2-}–ZrO_2; WHSV = 0.36 h^{-1}; T = 573 K, H_2/n-C_4 = 6. Catalyst composition as mass ratio Pt/Al_2O_3 to SO_4^{2-}–ZrO_2: A-1, 0.0; B-1, 0.1; C-1, 0.2 (not shown to avoid blurring); D-1, 0.4; E-1, 0.6; F-1, 0.8 and G-1, 1.0; F-1; and G-1 are not shown because they overlapped with E-1.

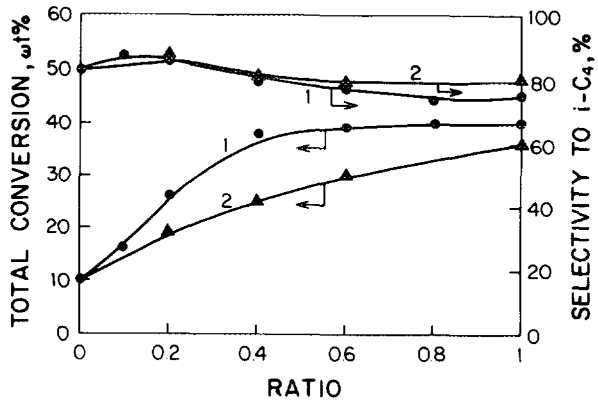

FIG. 5. Stable values (4 h on stream) of total conversion of *n*-C_4 and selectivity to *i*-C_4, as a function of the mass ratio Pt/Al_2O_3 to SO_4^{2-}–ZrO_2. WHSV = 0.36 h^{-1}; T = 573 K; H_2/n-C_4 = 6. (Curve 1) catalysts A-1 to G-1 prepared calcining the mixture of both components at 893 K; (curve 2) catalysts H-2 to K-2 prepared calcining first SO_4^{2-}–$Zr(OH)_4$ at 893 K, cooling and then mixing with Pt/Al_2O_3.

It seems that the addition of Pt/Al_2O_3 to SO_4^{2-}–ZrO_2 enhances the conversion of *n*-C_4 as a result of the appearance of a bifunctional reaction mechanism, which could not be obtained by supporting Pt directly over sulfated zirconia. There is also an inhibition of the formation of coke precursors in the mechanical mixture, possibly due to the surface migration of activated hydrogen generated on Pt.

Ebitani *et al.* (8) found that Pt maintains a high state of oxidation in a hydrogen stream at 673 K when it is directly supported on SO_4^{2-}–ZrO_2. This is noticeable because for most Pt-supported catalysts, the metal is in the reduced state at temperatures below 673 K.

If a sulfur barrier covering the metallic phase of Pt/SO_4^{2-}–ZrO_2 were the cause of the hindrance of the bifunctional mechanism, this phenomenon should also appear in the mechanical mixtures Pt/Al_2O_3 + SO_4^{2-}–ZrO_2. The reason for the difference should be the strong metal–support interaction of Pt in Pt/SO_4^{2-}–ZrO_2. The Pt in the Pt/Al_2O_3 catalyst is reduced at 773 K during the preparation of the catalyst. When Pt/Al_2O_3 is mixed with SO_4^{2-}–ZrO_2 and calcined in air at 893 K (catalyst A-1 to G-1), Pt is likely to become oxidized. The question arises of whether the reduction at 573 K is enough to return it to the reduced state. When Pt/Al_2O_3 and SO_4^{2-}–ZrO_2 are calcined separately, and then mixed and reduced at 573 K before the catalytic test (samples H-2 to K-2), the results obtained are similar to those of samples A-1 to G-1, as shown for the stable values in Fig. 5. In both cases, the addition of the metallic phase triggers a bifunctional reaction mechanism that enhances the conversion of *n*-butane. The difference in conversion values for samples with equal mass ratio in Fig. 5 can be assigned to the adsorption of water in the manipulation: in the case of $Pt/Al_2O_3 + SO_4^{2-}-ZrO_2$ (samples H-2 to K-2), adsorption of water occurs during the mixing step which cannot be eliminated with the pretreatment at 573 K. This water produces a decrease in the concentration of Lewis acid sites and in the catalytic activity (14).

The coincidence in behavior quoted above indicates that Pt is in the same oxidation state in both kinds of mixtures. Since in the case of $Pt/Al_2O_3 + SO_4^{2-}-ZrO_2$ (samples H-2 to K-2), the starting substrate is a Pt/Al_2O_3 catalyst reduced at 773 K for 6 h and the mixture is reduced again at 573 K, the supposed state in discussion must be the metallic one. Therefore, it must be concluded that a reduction at 573 K is enough to reduce the Pt deposited on Al_2O_3 and obtain de/hydrogenating properties. As quoted by Ebitani *et al.* (8), this temperature is not enough in the case of Pt on $SO_4^{2-}-ZrO_2$ and a temperature higher than 673 K is required to reduce the metal. The exposure of $SO_4^{2-}-ZrO_2$ to a reducing atmosphere at higher temperatures would produce the reduction of SO_4^{2-} and the concomitant destruction of acid sites responsible for the isomerizing activity. It is interesting to recall that according to the preparation method the sulfur concentration on $Pt/SO_4^{2-}-ZrO_2$ is one order of magnitude higher than that on sulfided Pt/Al_2O_3.

CONCLUSIONS

—When Pt is supported on $SO_4^{2-}-ZrO_2$, the activity of the catalyst is not modified, thus indicating that active sites are likely to be the same for $Pt/SO_4^{2-}-ZrO_2$ and $SO_4^{2-}-ZrO_2$.

—Pt in the presence of hydrogen is capable of inhibiting the formation of coke precursors. It seems that $SO_4^{2-}-ZrO_2$ alone does not have this capability, or has it to only a limited extent.

—At 573 K, a minimum partial pressure of H_2 is needed in order to stabilize the $Pt/SO_4^{2-}-ZrO_2$ catalyst ($H_2/n\text{-}C_4 \geq 6$).

—The loss of de/hydrogenating capacity by Pt may be due to the method of preparation of $Pt/SO_4^{2-}-ZrO_2$. Under present conditions, the reduction at 573 K does not impart metallic properties to Pt due to a strong metal–support interaction, while this temperature is enough to produce the metallic function in Pt/Al_2O_3.

—The use of a support other than $SO_4^{2-}-ZrO_2$ for the anchoring of the metallic phase, i.e., Al_2O_3, allows the complete reduction of Pt at 573 K. In this way, the classical bifunctional mechanism can operate when Pt/Al_2O_3 is mixed with $SO_4^{2-}-ZrO_2$ and higher activity is obtained than in the case of $Pt/SO_4^{2-}-ZrO_2$ or $SO_4^{2-}-ZrO_2$.

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