

# Characterization of Transition-Metal Oxides Promoted with Oxoanions by Means of Test Reactions

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The catalytic activity of some transition-metal oxides known to develop strong acidity by promotion with oxoanions was compared with a set of acid-catalyzed test reactions (isomerization of *n*-butane, isobutene, *n*-hexane, and cyclohexane). They were further characterized by thermally programmed desorption of pyridine and 2,4,6-trimethylpyridine, X-ray diffraction, and sorptometry.  $\text{SO}_4^{2-}\text{-ZrO}_2$ ,  $\text{SO}_4^{2-}\text{-TiO}_2$ ,  $\text{SO}_4^{2-}\text{-Fe}_2\text{O}_3$ ,  $\text{WO}_3\text{-ZrO}_2$ ,  $\text{WO}_3\text{-TiO}_2$ ,  $\text{WO}_3\text{-Fe}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3\text{-ZrO}_2$ ,  $\text{B}_2\text{O}_3\text{-TiO}_2$ , and  $\text{B}_2\text{O}_3\text{-Fe}_2\text{O}_3$  were synthesized by impregnation of the oxoanion over a fresh xerogel of the transition-metal hydroxide. Certain promoter-dependent orders, irrespective of the support, could be elucidated, mainly that the number of acid sites generated by promotion follows the order  $\text{S, W} > \text{B}$ . The proportion of strong acid sites is most important for S and B. The most active catalysts are always the zirconia ones, while the  $\text{Fe}_2\text{O}_3$  catalysts are the least active.

## 1. Introduction

Solid acids have been extensively used as catalysts or catalyst supports in the chemical industry, particularly in the petroleum field. Some transition-metal oxides, such as  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , and  $\text{Fe}_2\text{O}_3$ , have developed strong acidity after being surface doped with polyoxoanions (sulfate, tungstate, borate) and have been intensively studied because of their good activity level for hydrocarbon conversion, even at low temperatures, and their good selectivity for isomerization.<sup>1</sup> The literature is plentiful with data on the application of these acid catalysts to some specific reacting systems. The most detailed studies have dealt with the most active member of the family, sulfated zirconia<sup>2</sup> ( $\text{SO}_4^{2-}\text{-ZrO}_2$ , SZr). This material has attracted the interest of many researchers during the past decade, due to its superior properties for the activation of light alkanes.<sup>3,4</sup> Its high activity at low temperatures makes it an attractive candidate for substituting some corrosive liquids used in acid-catalyzed refinery reactors. Its industrial use is currently restricted to the isomerization of  $\text{C}_5\text{-C}_6$  paraffinic cuts for enhancing the octane number of gasoline.<sup>5-7</sup>

Test reactions are used to assess the properties of catalytic functions in a material. To characterize the acid or metal function, it is common to use probe molecules that under certain reaction conditions are very selective and yield only a small number of products. In many cases catalytic activity can be used as a measure of acidity and acid strength.<sup>8</sup> For most strong acid catalysts test reactions have been extensively used.<sup>9</sup> However, in the case of the catalysts based on oxoanion-promoted transition metal oxides there is not much comprehensive information about the activity of each oxoanion-support combination in elemental test reactions such as skeletal branching, double-bond isomerization, ring contraction, cracking, etc. Moreover, little is known about the role of each support and acidity promoter over the catalytic activity.

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The objective of this work was not to establish which were the absolute orders obtained under the optimum set of synthesis, pretreatment, and reaction conditions of each catalyst-reactant system. Such an approach not only would require too large a set of experimental data but would be scarcely useful for comparative purposes. Instead, we intended to establish an ordering of intrinsic properties of some transition-metal oxides promoted with oxoanions, e.g. total acidity, acid strength, and amount of Lewis and Brønsted acid sites, and to relate them to the catalytic activity properties under similar reaction conditions. We also tried to obtain simple correlations between the acid properties of these materials and their activity and selectivity in a given reaction test. In this way we would determine whether the effect of the promoter on the activity is directly related to the modification of the acid properties or not.

## 2. Experimental Section

**2.1. Catalyst Preparation. 2.1.1. Supports.**  $\text{Zr(OH)}_4$  was prepared by precipitation from a solution of Zr oxychloride,  $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ , which was supplied by Strem Chemicals (99.98%). The salt, in the form of a white powder, was first dissolved in distilled water ( $10\text{ mL g}^{-1}$ ) at room temperature and the solution stirred for 30 min. Then a solution of  $\text{NH}_4\text{OH}$  (Merck, 33%) was added dropwise ( $0.5\text{ mL min}^{-1}$ ) with gentle stirring until a pH value of 10 was reached. The freshly precipitated gel was aged in its mother liquor at room temperature overnight. Then it was subjected to a series of washing-decanting cycles until the supernatant liquid gave a negative result on the chlorine test by the Mohr method ( $\text{AgCl}$  test). The gel was then filtered in a glass funnel with  $10\text{ }\mu\text{m}$  paper filter and dried at  $110\text{ }^\circ\text{C}$  overnight in a stove.

For the preparation of  $\text{TiO}_2$ , titanium tetrachloride (Merck, 99%, yellow liquid) was used as the main starting material without any further purification, and when not used, it was kept in a desiccator. Since the dissolution of  $\text{TiCl}_4$  in water is explosively exothermic

and generates orthotitanic acid  $[\text{Ti}(\text{OH})_4]$ , a calculated amount of  $\text{TiCl}_4$  was dissolved in distilled water in an ice-water bath in order to produce a 2 M solution. The solution was acidified to pH 2 with drops of concentrated HCl to promote the hydrolysis. This aqueous solution was then placed in a temperature-controlled bath at 30 °C. After being maintained at the same temperature for 1 h, the solution was treated with 2.5 M dilute  $\text{NH}_4\text{OH}$  until the pH value was 10. The reaction conditions were maintained for a period of 1 h. The precipitated titanium hydroxide/hydrous titanium oxide ( $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ ) was separated from the solution by using filtration and repeatedly washed with distilled water to remove chloride ions. The hydrous oxide was then dried at 110 °C overnight. The powder was then compacted and shaped into pellets in a press.

$\text{Fe}(\text{OH})_3$  was prepared in the same fashion as  $\text{Zr}(\text{OH})_4$ .  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was used as the salt precursor (Sigma-Aldrich, 99%). Iron hydroxide was precipitated from ferric chloride solution using  $\text{NH}_4\text{OH}$  at room temperature, and stirring was maintained for 30 min. The precipitated gel was washed several times with distilled water until no chloride ions were detected in the wash water (AgCl test), filtered, and then oven-dried at 110 °C overnight.

Finally all the catalysts were ground in a mortar and sieved to 35–80 mesh.

**2.1.2. Promoters.** The final content of each promoter was regulated in order to produce surface density values lower than or equal to the monolayer value. The monolayer value is the maximum cationic density of a layer of the promoter (S, W, and B) deposited on the surface of the support ( $\text{ZrO}_2$ ,  $\text{TiO}_2$ , or  $\text{Fe}_2\text{O}_3$ ) with the thickness of one atom (no stacked cations).

In the case of the sulfate the anion is adsorbed in growing amounts as the concentration of the acid is augmented, until a saturation value is obtained. The structure of the gel is not damaged at low  $\text{H}^+$  concentrations, but severe Zr leaching and dissolution with loss of surface area occurs at acid concentrations greater than 5 N.<sup>8</sup> An optimum of 1–2 N has been reported by most authors. The final content of sulfate is regulated by the calcination treatments on the sulfated xerogel. Most authors agree that, for calcination temperatures of 600–650 °C, typical of the activation of sulfate-zirconia or sulfate-titania, surface sulfate contents stabilize at 2 S/nm<sup>2</sup> (half a monolayer) and the excess sulfate is decomposed to volatile  $\text{SO}_2$ .<sup>11</sup>

In the case of the heavier promoters, i.e., borate and  $\text{WO}_3$ , the excess quantities cannot be eliminated by heating, and therefore the initial content in the solid must be regulated in order to avoid pore blocking. In these cases, the most active catalysts for many acid-catalyzed reactions have promoter contents equal to or near the monolayer value. This monolayer value is similar to the surface cationic density of a plane of the crystal of high packing, e.g. (111). Experimental reported monolayer values for  $\text{WO}_3$  are 4.3 W nm<sup>-2</sup> (on alumina<sup>12</sup>) and 4.5–5.5 W nm<sup>-2</sup> (on zirconia<sup>13</sup>).

In contrast with alumina or silica supports, which are fairly sintering-resistant oxides,  $\text{Ti}(\text{OH})_4$ ,  $\text{Zr}(\text{OH})_4$ , and  $\text{Fe}(\text{OH})_3$  crystallize at fairly low temperatures when unpromoted (350–400 °C) and at moderate temperatures when promoted (500–700 °C). During crystallization high ionic mobility results in sintering and loss of surface area. Therefore, the amount of promoter to be initially impregnated in order to obtain a monolayer

**Table 1. Catalyst Properties**

catalyst	promotion <sup>a</sup>	S, W, B (%)	sg (m <sup>2</sup> g <sup>-1</sup> )	% phase/ % crystallinity
$\text{SO}_4^{2-}$ -ZrO <sub>2</sub> (SZr)	IE	1.3	120	50/68
$\text{WO}_3$ -ZrO <sub>2</sub> (WZr)	pH 6 (IE)	9.2	55	58/78
$\text{B}_2\text{O}_3$ -ZrO <sub>2</sub> (BZr)	pH 10 (IW)	1.0	109	100/33
$\text{SO}_4^{2-}$ -TiO <sub>2</sub> (Sti)	IE	0.3	23	89/95
$\text{WO}_3$ -TiO <sub>2</sub> (WTi)	pH 10 (IW)	3.0	18	35/85
$\text{B}_2\text{O}_3$ -TiO <sub>2</sub> (Bti)	pH 10 (IW)	0.2	18	72/86
$\text{SO}_4^{2-}$ -Fe <sub>2</sub> O <sub>3</sub> (SFe)	IE	0.5	52	-/98
$\text{WO}_3$ -Fe <sub>2</sub> O <sub>3</sub> (WFe)	pH 10 (IW)	4.2	25	-/92
$\text{B}_2\text{O}_3$ -Fe <sub>2</sub> O <sub>3</sub> (BFe)	pH 10 (IW)	0.1	11	-/98

<sup>a</sup> IE = impregnation with an excess of solution. IW = incipient wetness impregnation (the solution volume is made equal to the pore volume of the catalyst).

content cannot be determined directly but is to be determined experimentally. From the viewpoint of catalytic activity it has been reported<sup>14,15</sup> in the case of zirconia that active catalysts are produced with 15% W and 18% B. Given the typical values of specific surface area of tungsten-zirconia and boron-zirconia catalysts, these percentages exceed the monolayer value. In this work, promoter loadings were obtained by multiplying the initial area of the support by the reported monolayer density of the promoter (6 S nm<sup>-2</sup>, 5 W nm<sup>-2</sup>, 6 B nm<sup>-2</sup>).

The catalysts were calcined in air (10 mL min<sup>-1</sup>) at 800 °C in the case of the tungsten-promoted catalysts and 600 °C in the case of the sulfur- and boron-promoted catalysts. These values correspond to the temperatures of maximum activity in acid-catalyzed reactions for sulfate-, borate-, and tungsten-promoted zirconia.

**2.2. Catalyst Characterization. 2.2.1. Specific Surface Area.** The specific surface area (BET method), total pore volume, and pore size distribution (BJH method) were determined by nitrogen adsorption. The catalyst samples were degassed at 200 °C for 2 h, and then the nitrogen adsorption isotherm was determined at 77 K. A Micromeritics 2100E instrument was used for the experimental measurements.

**2.2.2. X-ray Diffraction.** The XRD measurements were performed in a Shimadzu XD-1 diffractometer with Cu K $\alpha$  radiation filtered with Ni and equipped with a pretreatment camera. Spectra were recorded in the 20–65° 2 $\theta$  range and with a scanning rate of 1.2° min<sup>-1</sup>. The content of the tetragonal phase of  $\text{ZrO}_2$  (see Table 1) was calculated using<sup>16</sup>

$$X_t (\%) = 100\alpha I_t / (I_m + \alpha I_t) \quad (1)$$

where  $X_t (\%)$  = content of the tetragonal phase,  $\alpha = 0.81$ ,  $I_t$  = integrated intensity corresponding to the (111) tetragonal peak, and  $I_m$  = sum of the integrated intensities of the (111) and (11-1) monoclinic peaks.

The content of the anatase phase in the  $\text{TiO}_2$  catalysts (Table 1) was assessed by means of<sup>17</sup>

$$X_a (\%) = 100 / (1 + K(I_r/I_a)) \quad (2)$$

$$K = (I_a/I_r)(W_a/W_r) \quad (3)$$

where  $W_a$  = weight of the anatase phase,  $W_r$  = weight of the rutile phase,  $I_a$  = intensity of the anatase phase, and  $I_r$  = intensity of the rutile phase. The results indicated that in the case of the iron oxide based catalysts there were many phases that could not be properly resolved, and for this reason no equations are included to calculate the fraction of each one.

**Table 2. Screening of Impregnation Conditions of B and W Precursors: Zirconia Catalysts**

catalyst	pH	method	% B or W	main species <sup>a</sup>	surface area (m <sup>2</sup> g <sup>-1</sup> )	acidity (μmol g <sup>-1</sup> )		<i>n</i> -butane conversn, %		isobutene conversn, %	
						total	strong <sup>b</sup>	1° pulse	20° pulse	1° pulse	20° pulse
BZr	4	IW	7	B(OH) <sub>3</sub>	36.6	310	23.8	0.3	0.0	35	9
	4	IW	4	B(OH) <sub>3</sub>	101	38	10.2	12	0.8	62	49
	7	IW	4	B <sub>3</sub> O <sub>3</sub> (OH) <sub>4</sub> <sup>-</sup>	112	37	11.5	0.6	2.1	61	15
	10	IW	4	B(OH) <sub>4</sub> <sup>-</sup>	109	400	151.4	13.4	1.4	27	2
WZr	6	IE	15	H <sub>2</sub> W <sub>12</sub> O <sub>42</sub> <sup>10-</sup>	55	720	48.0	5	0.0	42	5
	10	IW	15	WO <sub>4</sub> <sup>2-</sup>	52	400	24.1	0.4	0.0	33	4

<sup>a</sup> Main ionic species in the bulk solution. Taken from ref 20 (tungstates) and ref 21 (borates). <sup>b</sup> Pyridine molecules desorbing at temperatures higher than 500 °C.

**2.2.3. Temperature-Programmed Desorption of Probe Molecules.** The amount of acid and the acid strength were assessed by means of temperature-programmed desorption of probe molecules. 2,4,6-Tri-methylpyridine (TMP, collidine, Merck, synthesis reagent, >98% by GC assay) was used as a probe for Brønsted acid sites,<sup>18</sup> and pyridine (Merck, >98%) was used to test both Brønsted and Lewis acid sites. The samples were first immersed in an excess volume of the pure reactants at room temperature for 6 h. Then they were filtered and dried in still air in an open vial at room temperature. The samples were placed in a quartz microreactor and stabilized in N<sub>2</sub> for 1 h at 100 °C. Then they were heated from this temperature to 650 °C at 10 °C min<sup>-1</sup>. The desorbed products were continuously analyzed in a FID detector.

**2.2.4. Chemical Analysis.** The chemical analysis of S was performed by combustion and IR absorption in a LECO instrument. B analysis was performed by ICP after digesting the sample with HF. The W content was determined by X-ray fluorescence.

**2.2.5. Test Reactions.** Before the test, the catalysts were activated (removal of adsorbed water) by passing air (5 mL min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>) at 500 °C for 1 h. Then they were cooled in nitrogen to the desired reaction temperature.

**2.2.5.1. Isobutene Isomerization.** This was performed in a pulse reactor. Pulses of the reactant (0.3 mL per pulse, isobutene, 99.99%, Matheson Gas Co.) were injected into a N<sub>2</sub> stream (8 mL min<sup>-1</sup>) which flowed over a sample of the catalyst (300 mg) maintained at 70 °C and 0.1 MPa. Before the test the catalysts were activated (removal of adsorbed water) by passing air (8 mL min<sup>-1</sup>) at 500 °C for 1 h. A 25% dimethylsulfolane (stationary phase) over Chromosorb P 1/8 in. o.d. packed column was used to chromatographically separate the products. This was a test for all kinds of acid sites. A decoupling of each family of reactive sites was tried by selectively poisoning with pyridine and desorbing at chosen temperatures (200, 400, and 600 °C).

**2.2.5.2. *n*-Butane Isomerization.** This was performed in the same way as the isomerization of isobutene. The only difference was that the reaction temperature was set at 200 °C. *n*-Butane was supplied by AGA (99.9%).

**2.2.5.3. Cyclohexane Reaction.** The conversion of cyclohexane (Merck 99.9%) was performed at 300 °C, 0.1 MPa, catalyst mass 0.1 g, WHSV 10 h<sup>-1</sup>, and molar ratio H<sub>2</sub>/C<sub>6</sub>H<sub>12</sub> = 30. Methylcyclopentane was expected to be formed by isomerization on strong acid sites. The reaction products were analyzed by on-line chromatography with a packed column of FFAP supported on Chromosorb P.

**2.2.5.4. *n*-Hexane Reaction.** *n*-Hexane isomerization was performed in the continuous-flow mode. Reac-

tion conditions were as follows: temperature 200 °C, pressure 0.1 MPa, carrier 8 mL min<sup>-1</sup> of N<sub>2</sub>, WHSV = 0.8, catalyst mass 300 mg. *n*-Hexane was supplied by Merck (99.99%).

### 3. Results and Discussion

**3.1. Textural Properties and Promotion Conditions.** Table 1 shows some properties of the samples, promotion conditions, promoter content, specific BET surface area after calcination, and XRD results. After drying, xerogels of similar surface area were obtained in the case of Zr(OH)<sub>4</sub> (220 m<sup>2</sup> g<sup>-1</sup>) and Fe(OH)<sub>3</sub> (244 m<sup>2</sup> g<sup>-1</sup>). The Ti(OH)<sub>4</sub> xerogel had a lower surface area (72 m<sup>2</sup> g<sup>-1</sup>). The sulfation with excess solution produced, after calcination at 600 °C, surface contents close to half a monolayer (2 S nm<sup>-2</sup>). The S excess was thought to decompose to SO<sub>2</sub>, which was detected in the exhaustion gases during calcination.<sup>11</sup> The choice of the method of impregnation of B and W was made by first preparing samples impregnated at different pH values, comparing the values of surface area after calcination, and comparing the activity in the reactions of *n*-butane and isobutene (see Table 2).

The pH governs two opposing phenomena. (i) The first is the surface charge of the support, which changes its sign upon crossing the zero point of charge (ZPC) and varies between pH 6 and 8 for ZrO<sub>2</sub>, TiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>.<sup>19</sup> At pH < ZPC the charge is positive and the cations are repelled. At pH > ZPC the charge is negative and the anions are repelled. (ii) The second is the degree of oligomerization of the anion, which in the case of W and B mainly decreases at high pH values (see Table 2). Bulky oligomers, such as B<sub>3</sub>O<sub>3</sub>(OH)<sub>4</sub><sup>-</sup> and H<sub>2</sub>W<sub>12</sub>O<sub>42</sub><sup>10-</sup>, diffuse with difficulty or block the porous structure. Four pH values were tried for B, because it has non-negligible concentration values of small ions in a wide pH range. Only two pH values were tried for tungsten (6 and 10) because acidic pH values decrease the solubility too much and thermodynamically favor only bulky oligomers in solution.

In the case of boron no regular patterns of area, acidity, and activity were obtained that could determine about the dominance of (i) or (ii) on varying pH conditions. The synthesis pathway at pH 10 was chosen on the basis of the higher activity in *n*-butane isomerization and the greater concentration of strong acid sites. In the case of W it seems that the most important factor is the charge of the support (i). Higher values of acidity and amounts of strong acid sites are found at low pH values.

Both B and W were impregnated in a quantity equal to the surface cationic density of the corresponding promoter oxide (5.5 W nm<sup>-2</sup>, 5 B nm<sup>-2</sup>) multiplied by the surface area of the support before calcination. If a

**Table 3. Catalysts and Their Acid Contents, Brønsted Acidity As Measured by Desorption of Trimethylpyridine, and Total Acidity As Measured by Desorption of Pyridine and Amount Desorbed at Different Temperature Intervals**

catalyst	acidity ( $\mu\text{mol m}^{-2}$ )							
	Brønsted	total	0–200 °C	200–300 °C	300–400 °C	400–500 °C	500–600 °C	>600 °C
SZr	8.6	11.9	0.22	2.64	4.05	0.12	3.63	1.22
WZr	3.0	8.4	0.001	3.45	2.29	1.74	0.8	0.07
BZr	3.5	3.8	0.02	0.27	0.51	0.65	0.69	0.69
STi	2.3	3.7	0.15	0	0	1.47	2.04	0.03
WTi	0.4	0.7	0.05	0.15	0.06	0.19	0.11	0.13
BTi	0.5	0.6	0.04	0.09	0.04	0.14	0.13	0.17
SFe	1.0	2.2	0.01	0.04	0.04	0.03	0.06	0.03
WFe	0.1	0.1	0	0.04	0.03	0.01	0	0
BFe	0.1	0.2	0.001	0.01	0	0.09	0	0.1

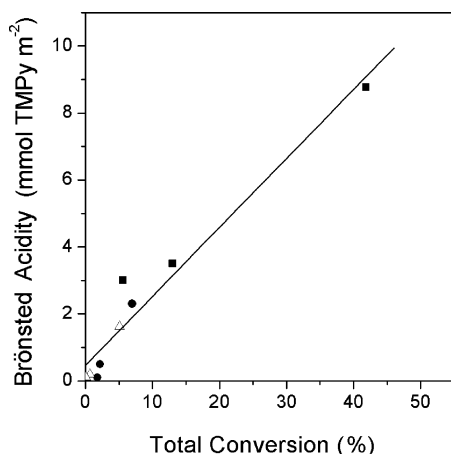
drop of the specific surface area occurred, it was thought that this was due to the aggregation of B and W species not homogeneously dispersed.

Promotion of  $\text{Zr}(\text{OH})_4$  with oxoanions and subsequent calcination mainly produced the appearance of its metastable tetragonal crystal phase. In the absence of the promoter the dominant phase is the thermodynamically stable one, monoclinic. The  $\text{TiO}_2$  catalysts were stabilized mainly in the anatase phase. The other main component was the rutile phase.

The  $\text{Fe}_2\text{O}_3$  catalysts had a mixture of many phases: goethite, hematite, and others that could not be adequately resolved.

**3.2. Temperature-Programmed Desorption.** Table 3 shows the values of total acidity expressed as the amount of pyridine desorbed per unit surface area of the catalysts and the Brønsted acidity, expressed as the amount of trimethylpyridine desorbed per unit surface area of the catalysts. The pyridine TPD results allow some general trends to be found. Irrespective of the support chosen, sulfate promotion produces the greatest amount of acid sites per unit area, which is greater than that produced by W or B. Total acidity decreases according to the order  $S > W > B$ . The trimethylpyridine-TPD results reveal a different order for the Brønsted acidity of the samples:  $S > B > W$  (shown in Figure 1).

Table 3 also shows the acid strength distribution of samples expressed as the amount of pyridine desorbed at different temperature intervals. It can be seen that S and B mainly generate sites of medium and high strength, while W mainly generates sites of medium and weak strength. If we now turn our attention to the influence of the support for a given promoter, it can be



**Figure 1.** Correlation between Brønsted acidity of the catalysts and the conversion of *n*-butane: (■) S/Z, W/Z, B/Z; (●) S/Ti, W/Ti, B/Ti; (△) S/Fe, W/Fe, B/Fe.

**Table 4. Results of the *n*-Butane and *n*-Hexane Reaction Tests: Initial Conversion (X, %) and Selectivity (%)<sup>a</sup>**

catalyst	<i>n</i> -butane		<i>n</i> -hexane				
	X	i-C <sub>4</sub>	X	C <sub>1-2</sub>	C <sub>3-5</sub>	i-C <sub>6</sub>	i-C <sub>7</sub>
SZr	43	64	9.0	0	74	26	0
WZr	5	79	3.6	0	83	17	0
BZr	13	58.6	4.7	0	78	22	0
STi	7	80	2.1	0	13	49.5	37.5
WTi	1.8	74	1.54	71	0	29	0
BTi	2.2	67	1.8	50	0	50	0
SFe	5.5	67	1.56	44.9	0	56.1	0
WFe	0.2	100	1.1	50	0	50.0	0
BFe	0.0	100	1.2	53	0	47.0	0

<sup>a</sup> The first pulse in the case of the *n*-butane test and 5 min for the first sample in the case of the *n*-hexane reaction.

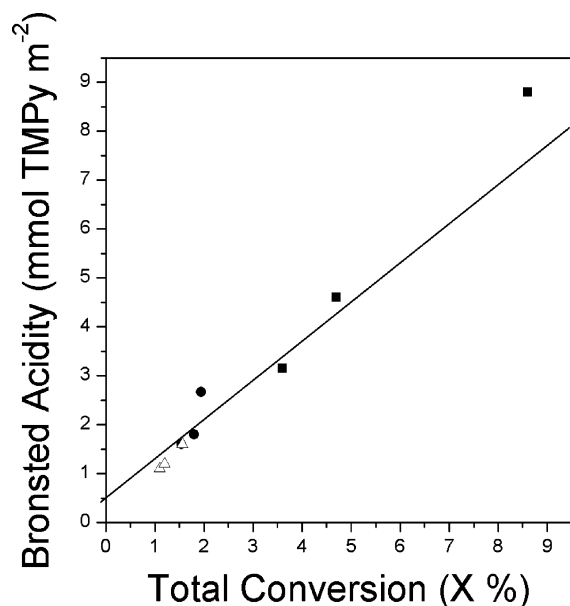
seen that  $\text{ZrO}_2$  produces the greatest amount of acid sites, followed by  $\text{TiO}_2$ . Promotion of  $\text{Fe}_2\text{O}_3$  produces the lowest amount of acid sites. In summary, in this case the order is  $\text{Zr} > \text{Ti} > \text{Fe}$ .

We can therefore conclude that, for this family of oxoanion-promoted transition-metal oxides, the kind of generated acid site, its surface concentration, and its acid strength all depend on the kind of support or promoter involved. The promotion of the same support with different promoters generates sites of different type (Brønsted or Lewis) and of different acid strength distribution.

The differences in acidity generation are difficult to rationalize with simple models. All the central cations of the promoting polyoxoanions have a higher electronegativity ( $\chi$ ) than the cation of the support:<sup>22</sup>  $\chi(\text{Zr}^{4+}) = 11.9$ ,  $\chi(\text{Ti}^{4+}) = 13.9$ ,  $\chi(\text{Fe}^{3+}) = 13.8$ ,  $\chi(\text{S}^{6+}) = 33.5$ ,  $\chi(\text{B}^{3+}) = 14.3$ ,  $\chi(\text{W}^{6+}) = 30.7$ .

Upon promotion with S, B, and W an increase of the electron deficiency of the Zr, Ti, and Fe surface cations of the support, and therefore of the surface acidity, can be expected on the basis of the polarization of the central cation ( $\text{Ti}^{4+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zr}^{4+}$ ). The greater acidity generated by sulfur addition can be explained by the high electronegativity of sulfur and the sulfate ion and the homogeneous surface dispersion achieved by S impregnation.

**3.3. Catalytic Tests.** Results corresponding to the reaction of *n*-butane and *n*-hexane can be found in Table 4. Isomerization of *n*-butane is commonly regarded as a reaction demanding the presence of strong acid sites. Strong acid sites are considered those that desorb pyridine at  $T > 500$  °C. The *n*-butane conversion level seems to be related to the amount of strong acid sites of each catalyst. With respect to the support, the order of catalytic activity is  $\text{Zr} > \text{Ti} > \text{Fe}$ . The conversion values for each support follow approximately the order  $S > B > W$ . The results indicate that the activity does not correlate with the total amount of acid sites, though it does correlate with the total amount of Brønsted acid



**Figure 2.** Correlation between Brønsted acidity and the conversion of *n*-hexane: (■) S/Z, W/Z, B/Z; (●) S/Ti, W/Ti, B/Ti; (△) S/Fe, W/Fe, B/Fe.

sites. If we relate the total amount of TMP desorbed with the conversion values of each sample, a linear plot is obtained, as can be seen in Figure 1. The activity in *n*-butane isomerization reaction is then directly related to the total amount of Brønsted acid sites of each sample. On average the W catalysts were more selective to isobutane, a fact surely related to their distribution of acid sites. The S and B catalysts had a greater yield of cracking, oligomerization, and dismutation products, though this yield of degradation products decreased with time on stream (pulse number), very likely because of deactivation by coking of the stronger acid sites.

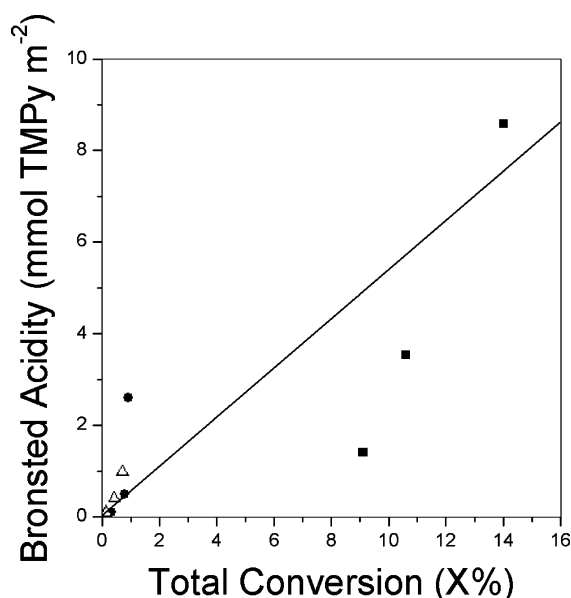
In the case of the isomerization of *n*-hexane, the catalytic activity order with respect to the support is the same found for *n*-C<sub>4</sub>: Zr > Ti > Fe. When the influence of the promoters is analyzed, the activity order is again S > B > W. As was the case with the *n*-butane results, a linear relation can be obtained when we relate the total amount of TMP desorbed with the conversion values of each sample (see Figure 2). Despite the similarities, some differences between the *n*-butane and *n*-hexane reaction results are found when the selectivity values are compared. In the case of the *n*-hexane reaction, all the Zr catalysts have a similar distribution of products, with low selectivity to isohexanes and a dominance of C<sub>3–5</sub> products. In the case of the Ti and Fe catalysts a higher selectivity to isohexanes is apparently related to the low conversion values. These materials showed also a high selectivity to deep cracking products. The variations in the product selectivities cannot be explained easily by invoking the total acidity or the acid distribution of each catalyst.

The results obtained with the cyclohexane isomerization reaction test are included in Table 5. The activity order considering the promoters is again S > B > W. With respect to the support, the activity order is again Zr > Ti > Fe. C<sub>6</sub> isoparaffins (ring-opening products with no further cracking) are solely produced by SZr and WZr. It seems strange that BZr, which has more strong acid sites than WZr, does not open the cyclohexane ring. It is also strange that some samples produce cracking products but no hexane isomers. C<sub>1–5</sub> would

**Table 5. Cyclohexane Test Reaction: Conversion and Selectivity Values<sup>a</sup>**

catalyst	conversion (%)	selectivity (%)			
		ROP			
		MCP	C <sub>6</sub> isomers	C <sub>4</sub> –C <sub>5</sub>	C <sub>1</sub> –C <sub>3</sub>
SZr	14.2	97.0	1.9	0.8	0.3
WZr	9.1	75.4	19.1	5.0	0.6
BZr	10.6	99.5	0.1	0.2	0.2
STi	0.75	93		7	
WTi	0.9	77		23	
BTi	0.3	70	26	3	1
SFe	0.3	100			
WFe	0.1	33		25	42
BFe	0.25	4.6	6.3	89.1	

<sup>a</sup> Legend: ROP = ring-opening products; MCP = methylcyclopentane.



**Figure 3.** Correlation between Brønsted acidity and the conversion of cyclohexane: (■) S/Z, W/Z, B/Z; (●) S/Ti, W/Ti, B/Ti; (△) S/Fe, W/Fe, B/Fe.

**Table 6. Reaction of Isobutene over Fresh, Undoped Catalysts: Initial Conversion and Selectivity Values (First Pulse)**

catalyst	conversion (%)	selectivity (%)	
		C <sub>4</sub>	C <sub>1–3</sub> + C <sub>5</sub>
SZr	70	64	36
WZr	60	57	43
BZr	58	40	60
STi	30	45	35
WTi	12	37	63
BTi	9.8	9	91
SFe	25	25	75
WFe	5.0	69	31
Bfe	5.1	59	41

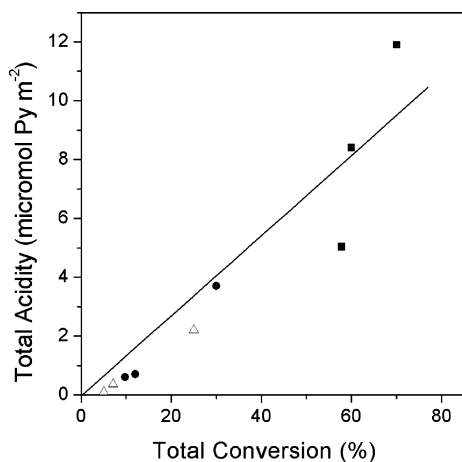
be produced by cracking of C<sub>6</sub> isomers coming from the ring opening of cyclohexane. The conversion values were compared with the total acidity, the Brønsted acidity, and the Lewis acidity. No relation between conversion and acidities could be found in this case. As an example, Figure 3 shows the lack of correlation between the Brønsted acidity and the conversion of cyclohexane.

Isobutene isomerization was performed both on fresh catalysts and on catalysts partially doped with pyridine. In the case of the fresh catalysts (Table 6) the activity order considering the support influence is again Zr > Ti > Fe, but the differences are less pronounced. When

**Table 7. Reaction of Isobutene: Catalysts Doped with Pyridine and Heat-Treated at Different Temperatures in Flowing N<sub>2</sub> (10 mL min<sup>-1</sup> g<sup>-1</sup>) in Order to Desorb the Base**

catalyst	desorpn at 200 °C			desorpn at 400 °C			desorpn at 600 °C		
	conversion (%)	selectivity(%)		conversion (%)	selectivity (%)		conversion (%)	selectivity (%)	
		C <sub>4</sub>	C <sub>1-3</sub> + C <sub>5-6</sub>		C <sub>4</sub>	C <sub>1-3</sub> + C <sub>5-6</sub>		C <sub>4</sub>	C <sub>1-3</sub> + C <sub>5-6</sub>
SZr	2.5	0	100	46	7	93	70	53	47
WZr	0.46	0	100	58	13.2	86.8	60	44	56
BZr	0	0	0	44	9.6	90.4	58	39	61

we consider the promoter influence, the activity ordering is S > W, B. When we attempted to correlate the conversion values with the acidity of the catalysts, it was found that a linear correlation existed between the total conversion and the total acidity, as plotted in Figure 4. The conclusion is clear: all the acid sites participate in the reaction.



**Figure 4.** Correlation between total acidity (pyridine desorbed per unit surface) and the conversion of isobutene: (■) SZr, WZr, BZr; (●) S/Ti, W/Ti, B/Ti; (△) S/Fe, W/Fe, B/Fe.

The experiments of partial poisoning with pyridine were aimed at elucidating the contribution to the activity of groups of sites of different acid strength. The activation of olefins can proceed even over sites of very weak strength. On the very strong acid sites fast coke formation and deactivation can also occur. Deactivation can be due to irreversible chemisorption at the low temperature of the test (70 °C). SZr has indeed been reported to act as a trap for olefins at room temperature.<sup>23</sup>

The results of Table 7 indicate that all the sites participate in the reaction: those of low, medium, and high acid strength. In the case of WZr and BZr, these catalysts practically do not have any sites desorbing pyridine between 0 and 200 °C (weak, Table 3), and therefore, their activity after desorbing pyridine in this range is practically null. SZr has a greater amount of weak acid sites (0.22 micromol m<sup>-2</sup>) and has the highest isobutene conversion after desorbing pyridine at 200 °C. WZr recovers practically all its activity after desorption at 400 °C, because this catalyst has mainly sites of medium acid strength. SZr and BZr, which have mostly sites of medium and high strength, recover about 70% of their original activity upon pyridine desorption at 400 °C and practically 100% at 600 °C.

#### 4. Conclusions

In the case of the oxoanion-promoted transition-metal oxides, the conversion level for different acid-catalyzed reactions depends mostly on the amount, type, and strength of the acid sites. The kind of generated acid site, its surface concentration, and its acid strength depend on the support and the promoter. Promotion with S and B produces mainly medium and high strength acid sites with similar catalytic properties. W promotion produces mainly sites of low and medium acidity of low cracking activity. The production of acid sites follows the trends S > W > B and Zr > Ti > Fe.

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