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Study of *n*-hexane isomerization on mixed Al_2O_3–ZrO_2/SO_4^{2-} catalysts

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Abstract

Mixed oxides of alumina and zirconia having a relative composition of 50, 80 and 100% Zr_2O were synthesized by means of sol–gel methods. The catalysts were sulfated with H_2SO_4 1N, and were loaded with 0.3% Pt metal using the incipient wetness technique. The characterization of the physicochemical properties was carried out using XRD, N_2-adsorption at 78 K, and SEM. The catalytic properties of the Al_2O_3–ZrO_2 series were studied by means of dehydration of 2-propanol at 180°C and isomerization of *n*-hexane at 250°C, 1 atm. The sulfated solids presented a high surface acidity and a limited crystallinity, together with high activity for alcohol dehydration (i.e. 2-propanol). On the other hand, the Al_2O_3–ZrO_2 solid solutions (i.e. those having a 20–80% composition) turned out to be the most active ones for the isomerization of *n*-hexane. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Al_2O_3–ZrO_2; *n*-Hexane; Isomerization

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1. Introduction

The industrial alkylation process to obtain high octane gasoline (i.e. RON > 94) uses liquid acid catalysts such as HF and H_2SO_4, which provoke serious problems related to corrosion, a negative environmental impact and potential risks (20 ppm HF is a lethal dose). This has motivated the search for alternative solid acid catalysts for obtaining the high octane gasoline without the inconveniences presented by the liquid acid catalysts. In this respect, the present work focused on the evaluation of the sulfated zirconia system, which has been reported to have the surface acidity required to promote acid-catalyzed reactions, for example for light paraffin alkylation and isomerization [1,2]. The microcrystalline zirconia solids generally have a low surface area and a high total surface acidity, i.e. about 20 m^2/g and more than 200 meq. (NH_3)/g, while alumina has a poor crystallinity, but at the same time it is a very porous material having a moderate surface acidity; then, it was postulated in this work that the incorporation of alumina into the zirconia phase could create a new mixed system having both surface area and acidity values in the medium range [2,3].

Previous reports by Guevara et al. [3] indicated that the sulfation procedure was important for obtaining acidic solids by means of the sol–gel method; in particular, the mixed oxides having a composition 20–80 wt.% Al_2O_3–ZrO_2, formed a solid solution when they are prepared by that method. Using three different procedures for sulfation: at the stage

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of homogenization or during the alkoxides hydrolysis, or even after drying the material. The sulfation of the solids by H_2SO_4 led to a surface area smaller than the pure Al_2O_3 sulfated with ammonium sulfate; however, the acid sites density of the former (i.e. 20–80% ZrO_2–Al_2O_3) was greater than pure alumina, as well as their catalytic activity for dehydration of 2-propanol [4]. In this work, a series of three catalysts consisting of Al_2O_3–ZrO_2 having a relative composition of 50–50, 20–80 and 0–100 wt.% were prepared and characterized with respect to their textural, structural and surface acidity properties, and their catalytic activity was measured in the dehydration of 2-propanol at 180°C and in the isomerization of *n*-hexane at 250°C, 1 atm.

2. Experimental

Zirconia–alumina mixed oxides were synthesized from zirconium propoxide and aluminum tri-sec-butoxide (Aldrich Co.), using isopropyl alcohol as a solvent. It was used as an alcohol/alcoxide ratio of 17 for the 50 and 80% ZrO_2 mixed oxides, and 20 for the 100% ZrO_2 sample; a water/alcoxide molar ratio of 40 was kept constant in all the cases. Synthesis of these materials was realized in a Pyrex glass reactor, where the reactants were added under an inert atmosphere. The mixture was stirred at room temperature for 1 h, and a certain amount of water was added for carrying out the hydrolysis, leading to the formation of a gel, which condensed at 60°C after 2 h, being aged for 24 h at room temperature. Solids thus obtained were dried at 120°C for 12 h, and calcined at 625°C for 4 h under a dynamic air atmosphere [3,4]. This series of solids had a composition of 50–50, 20–80 and 0–100% Al_2O_3–ZrO_2. The sulfation of these materials was accomplished by impregnating the dried supports with H_2SO_4 1N (3% S/g) [2]. Afterwards, samples were impregnated with 0.3 wt.% Pt, using an aqueous solution of chloroplatinic acid (Merck) and the incipient wetness technique.

The residual sulfur remaining after the impregnation step was determined by means of an elemental analyzer CHONS-Perkin-Elmer, Mod 2400. Analyses by SEM were realized by means of an electronic microscope TOP-COM, Mod SM-510. Identification of the crystalline phases and the crystallinity degree of the sol–gel materials were determined by means of a Rigaku DMAX-2200 diffractometer with a copper tube and a λ_B monochromator, while textural properties were measured by means of a Quantachrome Autosorb-1 apparatus. Density of acid sites and the total surface acidity were determined by means of potentiometry measurements using *n*-butylamine for titrating the acidic sites of medium and higher strength, according to data reported in the literature [5]. Relative acidity of the materials was also evaluated by means of a reaction test, using the 2-propanol dehydration in a continuous reactor system at 180°C, WHSV $= 0.5$/h, at 1 atm; the products coming out of the steel reactor were identified by means of on line GC. This test reaction was sensitive enough for detecting the surface acid and basic sites, being able to distinguish the acidic or basic character by means of the relative proportion of the products, i.e. propylene, di-isopropyl-ether (DIPE) and acetone.

The isomerization reaction of *n*-hexane was carried out in a continuous flow system using a glass reactor at 250°C, 1 atm, H_2 being used as a carrier gas. Each solid was submitted to a careful pretreatment for reducing the Pt complexes in situ, at 350°C in H_2 for 2 h, previous to the reaction. The reaction products were analyzed on line GC, using a Varian 3300 GC fitted with FID and a column packed with 23% SP-1700.

3. Results and discussion

X-ray diffraction profiles of the complete series AZ-50-S and AZ-80-S confirmed the presence of the crystalline phase of γ-alumina and a mixture of monoclinic and tetragonal zirconia phases. Tetragonal zirconia phase prevailed in the AZ-50-S and AZ-80-S mixed oxides [5]. AS-100 sample presented tetragonal and cubic zirconia phase, but when this sample was sulfated the cubic phase disappeared [6]. Diffractograms corresponding to these mixed oxides showed the characteristic peaks of zirconia phase, i.e. $2\theta = 30, 35^\circ$ (tetragonal phase), $2\theta = 28, 31^\circ$ (monoclinic phase), together with those corresponding to γ-alumina, i.e. $2\theta = 46$ and 67° [5–8]. However, increasing the concentration of the zirconia phase in the mixed oxides provoked a decrease of the peak intensity at $2\theta = 46^\circ$ (γ-alumina), which completely disappeared when the zirconia concentration reached

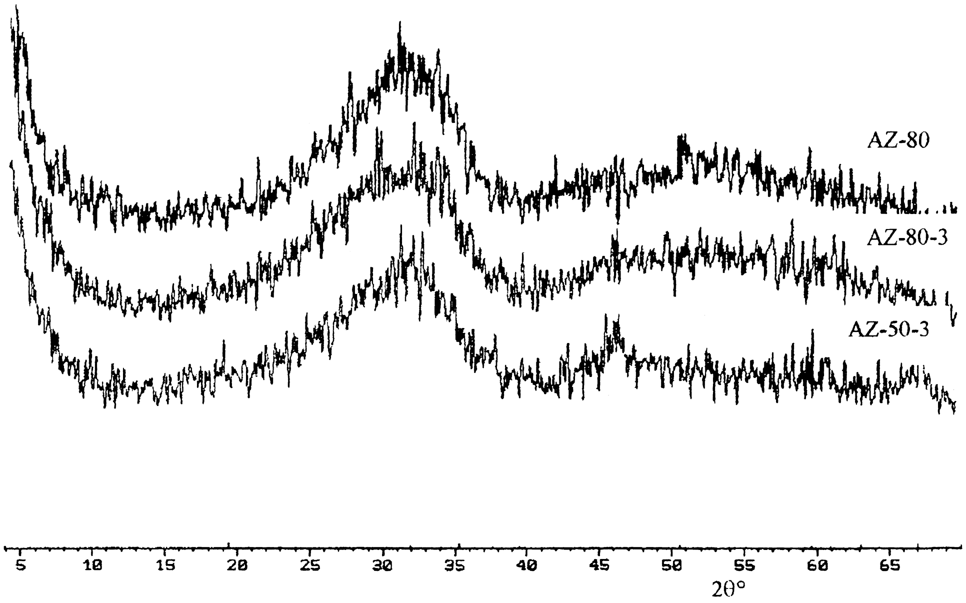

Fig. 1. X-ray diffraction patterns of mixed sulfated oxides Al_2O_3–ZrO_2.

80% (AZ-80-S). Sulfated solids presented a lower crystallinity, as indicated by the broad X-ray diffraction peaks (Fig. 1). It was observed that the residual sulfur in the catalysts varied according to the concentration of zirconia in the mixed oxides as we can see in Table 1, which contains the actual sulfur content for each catalyst, as well as the textural and acidic properties of the materials.

Table 1 shows that sulfur content varied according to the amount of zirconia in the mixed solids. That is, when the amount of zirconia is high, the actual amount of sulfur becomes closer to the nominal value (3%). Surface area corresponding to the non-sulfated catalysts diminished when the content of zirconia increased. However, for sulfated AZ-80-S and AZ-100-S samples, their surface area increased in relation to the corresponding non-sulfated ones, but the AZ-50 solid showed a reduction of its surface area upon sulfation. This surface area reduction is an effect already observed in zirconia–alumina mixed oxides with low content of ZrO_2 [5]. Pore volume diminished with sulfation of the samples, except for the AZ-100 solid, and they showed a bimodal distribution in pore size of 34 and 300–317 Å; these results are similar to those found by Armendariz et al. [6] and by Signoretto et al. [7] on sulfated zirconia. Table 1 also presents total acidity results obtained in the potentiometric titration with *n*-butylamine for the non-sulfated and sulfated

Table 1
Residual sulfur content, textural properties and acidity of the alumina–zirconia mixed oxides series

Catalyst	Actual content of S (wt.%)	Surface area (m^2/g)	Pore diameter (Å)	Pore volume (cc/g)	Acidity (mmol/g)
AZ-50	0	362	34 and 317	1.07	0.8
AZ-50-S	1.4	200	35 and 300	0.56	1.0
AZ-80	0	240	36 and 300	0.26	0.7
AZ-80-S	1.9	248	36 and 300	0.16	1.25
AZ-100	0	88	34 and 314	0.15	0.7
AZ-100-S	2.2	262	33 and 300	0.29	1.45

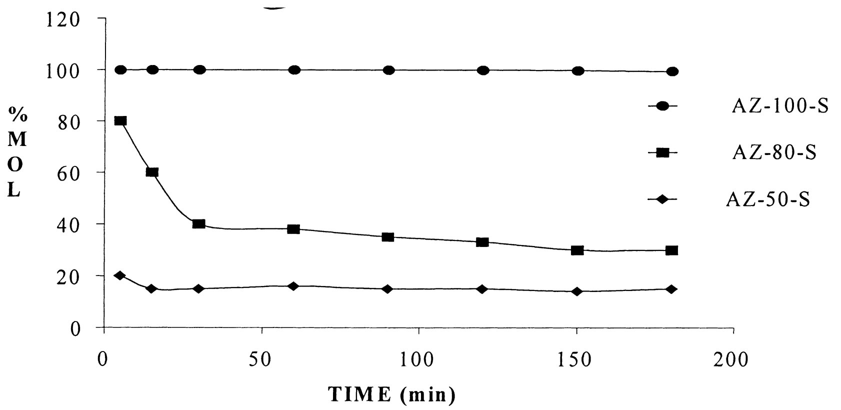

Fig. 2. 2-Propanol dehydration on alumina–zirconia mixtures.

materials. The presence of the sulfate ions increased the acidity of each catalyst and with the zirconia content in the mixed oxides, as well.

The relative acidity was tested indirectly by means of the dehydration of 2-propanol at 180°C, WHSV of 0.5/h, 1 atm. The results are condensed in Fig. 2.

Fig. 2 shows total conversion behavior obtained in 2-propanol dehydration on the three alumina–zirconia mixtures. In each of the catalyst propylene was the only reaction product observed, indicating the presence of acid sites only. However, AZ-100-S catalyst presented the highest transformation of 2-propanol which could be related to the highest acidity for this solid. An increase in the concentration of the alumina reduces significantly the acidity of the materials, as we can see in Table 1 and in previous works [3–5].

Table 2 shows catalytic activity data obtained for AZ-50-S, AZ-80-S and AZ-100-S in the isomerization of *n*-hexane at 250°C, 1 atm, $W/F = 0.25$/h after 60 min. These results indicate that mixed solid containing 80 wt.% ZrO_2 (AZ-80-S) presented higher conversion of *n*-hexane (18.5%) than the other two materials, with a minimum of light products, i.e. 10% of C_1–C_4 hydrocarbons. Pure zirconia (i.e. AZ-100-S) showed a significant total conversion together with the highest percentage of light products; this might be a consequence of the higher surface acidity presented by this solid, with respect to AZ-50-S and AZ-80-S.

Product distribution (Table 2) indicates that solid having 20–80 wt.% Al_2O_3–ZrO_2 are able to convert *n*-hexane towards C_6 isomers, i.e. 2,2-DMB, 2-MP and 2,3-DMB. There is a higher conversion to 2-MP on that catalyst (AZ-80-S), as well as an important diminution of cracking products compared with AZ-50-S and AZ-100-S; this could be related to its higher surface area and tetragonal zirconia phase content according to results found by other authors [6,7], who have attributed catalytic activity to the tetragonal phase, as well. On the other hand, catalysts AZ-50-S and AZ-100-S showed an increase of light products.

Results concerning the use of scanning electron microscopy of the alumina–zirconia solids showed important changes on the particle size when the concentration of zirconia was increased. More results will

Table 2
Catalytic activity of the sulfated alumina–zirconia series for the isomerization of *n*-hexane

Catalyst	Conversion of *n*-hexane (%)	Selectivity (%)			
		2,2-DMB	2-MP	2,3-DMB	Light products
AZ-50-S	4.3	8	25	24	43
AZ-80-S	18.5	2	54	34	10
AZ-100-S	13.4	0	18	14	68

appear in a future article. The electron microscopy study did not indicate specific modifications of morphology in the mixed oxide materials, even at low contents of ZrO_2.

4. Conclusions

Mixed oxides prepared by sol–gel methods, composed of alumina–zirconia promoted with sulfate, i.e. H_2SO_4, presented a surface acidity capable of promoting the isomerization of *n*-hexane. The intermediate acidity of the AZ-80-S solid promoted the isomerization of *n*-hexane, while the cracking products remained low. The additional acidity generated in these materials by the sulfates depended also on the amount of sulfur staying in the catalyst after sulfation. It is interesting to note that when the concentration of zirconia increased, the amount of sulfur reached a maximum which seems to be related to textural properties of the material. It was found that the amount of sulfur in the catalysts was related directly to the capacity of dehydration of 2-propanol. There is a substantial contribution of the alumina phase in the development of the surface area of the materials; for example, mixed oxides consisting of 20–80 and 50–50 wt.% Al_2O_3–ZrO_2 presented a superior surface area with respect to pure zirconia (AZ-100). On the other hand, sulfation of the AZ-100 sample had a positive effect on its textural properties, whereas the AZ-80 solid presented not an important increase in the surface area upon sulfation, and the AZ-50 sample showed a diminution on its textural properties. Further studies on the stability of the mixed solids during the catalytic reaction are necessary to improve the properties of the mixed oxides.

Acknowledgements

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