Zirconium-SAPO-11

The peculiar effect of zirconium addition on the catalytic properties for *n*-butene isomerization

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SAPO-11 and Zr-SAPO-11 solids were synthesized by hydrothermal methods and characterized. Zirconium is not incorporated in the SAPO-11 framework but is localized, at least partially, in the pores of the solid, inducing a partial pore blockage. When used in *n*-butene isomerization, both solids are active and selective but Zr-SAPO-11 exhibited higher isobutene selectivity as compared to SAPO-11. This improved isobutene selectivity for Zr-SAPO-11 catalyst is attributed to the presence of zirconium in the pores causing an increased shape selectivity.

Introduction

The skeletal isomerization of linear butenes has been investigated in depth in recent years and considerable information relating to catalyst activity and selectivity has been reported.¹⁻⁶

Among the catalysts which are known to have good catalytic properties are SAPO-11⁷ and MeAlPO-11, Me being either Co,⁸ Mn,⁹ Mg⁹ or Ge.¹⁰ The factors causing the high selectivity of these catalysts have not been fully identified. Some authors have pointed out the role of shape selectivity,¹¹ while others favour the importance of the acid strength of the acid centers.¹²

It has now been established, for zeolites, aluminophosphate materials and P–O–Si catalysts, that *n*-butene is selectively transformed into isobutene *via* a monomolecular mechanism, and to propene and pentene *via* a bimolecular mechanism.^{12,13} The monomolecular mechanism proceeds through a methylcyclopropyl carbenium ion, the active site being a proton located in the pores of the catalyst.¹⁴

An important factor affecting catalytic properties is the lifetime of the catalyst. Recently, it has been shown that hydrothermal dealumination of FER catalysts can increase their lifetime to more than one week.⁴

We report here on the peculiar effect of zirconium addition to a SAPO-11 catalyst on the catalytic properties of this material.

Experimental

Synthesis

SAPO-11 was synthesized as described in ref. 15, according to ref. 16. Zr-SAPO-11 was synthesized as follows. A homogeneous gel with the molar composition $1 \text{ Al}_2\text{O}_3 : 1 \text{ P}_2\text{O}_5 : 0.1$ SiO₂ : 0.1 ZrO₂ : 1 dipropylamine : 50 H₂O was pepared [all reactants from Aldrich, except pseudoboehmite (Catapal, Vista) and silica sol (Ludox)]. Pseudoboehmite (6.8 g) was added to a mixture of phosphoric acid (11.85 g H₃PO₄, 85%) and 45 g H₂O, under stirring at room temperature for 4 h. Zr(PrⁱO)₄ (1.63 g) was then added to the mixture. Then, 5 g of dipropylamine were added under stirring and 0.75 g of silica sol (AS 40) was subsequently added to the mixture.

After stirring the mixture for 1 h, it was transferred into a stainless-steel autoclave lined with Teflon which was sealed and heated at 473 K for 24 h. Both solids prepared, SAPO-11 and Zr-SAPO-11, were washed and then calcined in a flow of nitrogen, T being increased from room temperature up to 873 K. After 12 h at 873 K, the samples were flushed with oxygen, and then heated again at this temperature for 12 h. The resulting solids were used for characterization purposes or for the study of their catalytic performances.

Characterization

Products were characterized by X-ray powder diffraction (XRD; Philips W 1050 powder diffractometer) fitted with Cu-K α radiation, scanning electron microscopy (SEM; Hitachi S 800) and IR spectroscopy (Perkin-Elmer 580 FTIR spectrometer). Chemical compositions were determined by atomic absorption spectroscopy. Acidities of the samples were characterized by using temperature programmed desorption of ammonia (TPD of NH₃). ²⁷Al, ²⁹Si and ³¹P MAS NMR spectra were recorded at ambient temperature with a Bruker DSX 400 multinuclear spectrometer: spin speeds were *ca.* 5.5 kHz (²⁹Si), 12 kHz (²⁷Al and ³¹P), and the observed resonance frequencies were 79.5 MHz (²⁹Si), 104.2 MHz (²⁷Al) and 161.9 MHz (³¹P). Chemical shifts were recorded with respect to tetramethylsilane (TMS) for ²⁹Si, [Al(H₂O)₆]³⁺ for ²⁷Al and H₃PO₄ for ³¹P. Elemental analysis of the solids was performed by using atomic absorption measurements.

The porous volumes were measured by using *n*-hexane adsorption and a volumetric glass apparatus equipped with a MKS pressure gauge. For each sample an isotherm was recorded. The pore volume is defined as the adsorption volume at $P/P_0 = 0.1$.

Catalytic tests

The cataltyic properties of SAPO-11 and Zr-SAPO-11 were tested for n-butene skeletal isomerization by using a microflow reactor.

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 Table 1
 Chemical composition of the gel and solid products

	gel				solid products			
sample	Al	Р	Si	Zr	Al	Р	Si	Zr
SAPO-11 Zr-SAPO-11	21.60 20.58	24.80 23.63	1.12 1.07	3.47	21.24 21.93	24.10 22.01	1.22 0.98	3.27

The initial catalytic properties were determined for fresh non-aged materials. For this purpose, the solids were reacted with *n*-butene for 2 min, then the reactants were flushed with nitrogen for 5 min and then oxygen (30 min) and nitrogen again (10 min) before the next experiment. Reactant and products were analyzed by gas chromatography by using a Pona capillary column (Altech, France). The reaction temperature was fixed at 693 K and the butene pressure at 26 kPa, the complement to atmospheric pressure being nitrogen.

For the measurement of the initial catalytic properties, the WHSV (weight-hourly space velocity; weight of reactant per weight of catalyst) was adjusted to give low conversions. By contrast, to study the stability with time on stream, the WHSV was adjusted to give an initial conversion close to 40%.

The reactant was but-1-ene and the selectivity was calculated on a carbon basis considering all linear butenes (but-1-ene, *cis*- and *trans*-but-2-ene) as reactants. Conversion was defined as $(C_{\rm in} - C_{\rm out}/C_{\rm in}) \times 100$ with $C_{\rm in} =$ number of mol. of but-1-ene $C_{\rm out} = \sum$ but-1-ene + *cis*-but-2-ene + *trans*-but-2-ene. Isobutene selectivity is defined by the ratio of the number of moles of butenes transformed.

It has been reported that the *n*-butene isomerization reaction is sensitive to the acid sites located on the external surface of the zeolite crystals and to those located in the mesoporosity of the solid.¹¹ In order to obtain evidence for the possible presence of these sites, we have used the cracking of 2,2,4-trimethylpentane, a molecule which is known to have a kinetic diameter larger than the pore diameters of SAPO-11. Thus, the rate of 2,2,4-trimethylpentane cracking will depend on the number of external acid sites.

To study this reaction we used the bracketing technique: 3 min of reaction, then the sample was flushed with nitrogen for 5 min and oxidized in a flow of oxygen for 30 min at the reaction temperature which was fixed at 723 K. Under these experimental conditions, which result in conversions lower than 2%, the reproducibility is quite good.

Results

Chemical analysis results indicated that both samples have nearly the same Si contents and the chemical composition is given in Table 1.

The XRD patterns of Zr-SAPO-11 and SAPO-11 are given in Fig. 1. The XRD patterns are identical and indicate that the two solids have the AEL structure.¹⁷

The SEM results (micrographs of SAPO-11 and Zr-SAPO-11) are given in Fig. 2. There are no major differences, but it is observed that for SAPO-11 the average particle size is around 10 μ m, while it is close to 6–7 μ m for Zr-SAPO-11. For each sample, the large crystals are in fact composed of small crystallites of 0.5–1.5 μ m.

The samples (Zr-SAPO-11 and SAPO-11) were pressed into small wafers (*ca.* 20 mg), outgassed overnight at 773 K ($P = 10^{-3}$ Pa) and IR spectra were recorded at room tem-

perature. The spectra are reproduced in Fig. 3. Both solids exhibit the same OH vibrations. The IR vibration at 3740 cm^{-1} is due to terminal silanol groups, that at 3677 cm^{-1} attributed to P—OH vibrating species and the vibration at 3630 cm^{-1} to Brønsted acid sites.¹⁸ Therefore, the addition of zirconium to SAPO-11 does not create new types of hydroxy groups. The relative number of acid sites of Zr-SAPO11, as calculated from the absorbance of OH vibrations at 3630 cm^{-1} , is only half that of SAPO-11.

Results of ammonia TPD experiments are shown in Fig. 4. The sample was first treated under oxygen, T being increased from room temperature to 773 K and flushed by nitrogen before being cooled to 323 K. The solid was then contacted with ammonia pulses in order to saturate the surface. After being flushed with nitrogen, the ammonia TPD experiments were performed. Fig. 4 indicates that two TPD peaks are registered, the second peak being attributable to ammonia adsorbed on the strongest acid sites.¹⁵ From Fig. 4, it can be concluded that for both solids the acid strength is of the same magnitude (same maximum for the second TPD peak). The relative number of acid sites (area under the second TPD peak) of Zr-SAPO-11 compared to SAPO-11 is close to 0.6, a value which is in reasonable agreement with that calculated from the IR spectroscopy results.

Isotherms were recorded at 295 K and the pore volume calculated for $P/P_0 = 0.1$. The pore volume is equal to 0.6 mmol g^{-1} for SAPO-11, in good agreement with values reported in the literature.¹⁹ By contrast, for Zr-SAPO-11 the pore volume is 3.3 times smaller than that of SAPO-11.



Fig. 1 XRD spectra of (a) SAPO-11 and (b) Zr-SAPO-11



Fig. 2 Micrographs of (a) SAPO-11 and (b) Zr-SAPO-11

 27 Al MAS NMR spectra were obtained for both samples. A sharp resonance line centered at -36 ppm, due to tetrahedrally coordinated aluminium bound *via* oxygen to four P atoms,²⁰ is observed on both SAPO-11 and Zr-SAPO-11. For the two solids, an additional resonance at *ca*. 10 ppm is observed, probably due to octahedrally coordinated aluminium atoms of unreacted starting material²¹ (spectra not reported here).

The ³¹P NMR spectra of the samples were also obtained. The sharp resonance line at *ca.* 29 ppm is assigned to tetrahedral P sites with neighbouring AlO_4 tetrahedra [P(4Al)].²² A small additional line was observed at *ca.* 23 ppm and has been attributed to P(3AlO₄, 1Al-OH).²²

The ²⁹Si MAS NMR spectra of the samples are given in Fig. 5(a). For SAPO-11 [Fig. 5(a)], a single resonance is observed at -92 ppm and is ascribed to tetrahedral silicon atoms bound *via* oxygen to four Al atoms [Si(4Al)].²³ Consequently, the silicon present in SAPO-11 is fully incorporated on phosphorus T sites of the aluminophosphate framework. So, each Si atom incorporated should create a Brønsted acid site. For Zr-SAPO, the spectrum is broader than that for SAPO-11 [Fig. 5(b)], the main resonance line being centered



Fig. 3 IR spectra of hydroxy groups of (a) SAPO-11 and (b) Zr-SAPO-11 $\,$

at -92 ppm and presumably a weaker resonance line exists at *ca.* -110 ppm. This result is confirmed by using H⁺ cross polarization [Fig. 5(c)]: the signal obtained is now symmetrical and centered at -92 ppm. Therefore it is concluded that for Zr-SAPO-11, most of the silicon is incorporated in the framework as isolated Si(4Al), but a part of the silicon forms Si-O-Si domains as has been observed for other SAPO structures.²⁴ The part of silicon belonging to Si-O-Si domains can be estimated as 30% of the total silicon. From this result, and the chemical analysis results, it can be estimated that the number of protons in Zr-SAPO-11 is smaller than in SAPO-11. The number of H⁺ (Zr-SAPO-11)/number of H⁺ (SAPO-11), as calculated from NMR results, is 0.7, in reasonable agreement with the values obtained from IR spectroscopy results (0.5) and from ammonia TPD results (0.6).



Fig. 4 Results of ammonia TPD for (a) SAPO-11 and (b) Zr-SAPO-11





Fig. 5 $\,^{29}\text{Si}$ MAS NMR spectra of (a) SAPO-11, (b) Zr-SAPO-11 and (c) Zr-SAPO-11 with H^+ cross polarization

Catalytic properties

n-Butene isomerization

Initial catalytic properties. To compare the initial catalytic properties of the fresh solids, the bracketing technique (see Experimental) was used. The changes in isobutene selectivity as a function of the butene conversion are shown in Fig. 6.

Both solids exhibited high initial selectivities, as compared to other medium-pore SAPOs (SAPO-31 or SAPO-41) or to TON or MTT zeolites;¹⁰ moreover, it is observed that Zr-



Fig. 6 *n*-Butene reaction at 693 K, $P(C_4H_8) = 26$ kPa, complement to atmospheric pressure provided by nitrogen. Change in isobutene selectivity (S_i) versus conversion (α) for (a) SAPO-11 and (b) Zr-SAPO-11.

SAPO-11 is more selective than SAPO-11. Since both solids exhibited acid sites having the same acid strength as shown above, the change in selectivity may be related to the reduced porosity of Zr-SAPO-11: pore volume measurements clearly indicated that there is a large decrease in pore volume for Zr-SAPO-11 and suggest that the channels of Zr-SAPO-11 are probably smaller than those of the corresponding SAPO-11. This decrease in pore dimensions may be due to the presence of Zr compounds, *e.g.* small patches of ZrO_2 inside the internal pores.

Ageing with time on stream. In order to compare the catalytic stability of the catalysts, the WHSV was adjusted for both solids in such a way that the conversions were close to 40%. In Fig. 7 the change in *n*-butene conversion and isobutene selectivity are plotted *versus* time on stream. It appears that the zirconium-based sample is much more stable than the corresponding SAPO-11.

Trimethylpentane cracking

The results of the rate of 2,2,4-trimethylpentane cracking are summarized in Table 2. For both solids, the major cracked



Fig. 7 *n*-Butene reaction at 693 K. Change in conversion (and in selectivity) as a function of time on stream for (a) SAPO-11 (WHSV = $6.3 h^{-1}$) and (b) Zr-SAPO-11 (WHSV = $3.3 h^{-1}$).

sample	rate of 2,2,4-trimethylpentane cracking/ μ mol h ⁻¹ (g solid) ⁻¹
SAPO-11 Zr-SAPO-11	$0.28 \\ 7 \times 10^{-3}$

T = 723 K, P(trimethylpentane) = 1.6 kPa, complement to atmospheric pressure being nitrogen.



Scheme 1

products are isobutane and a mixture, at the thermodynamic equilibrium, of butenes (*n* and iso); this result is as expected because of the following reaction scheme for 2,2,4-trimethylpentane cracking (Scheme 1) the reactivity of $iC_{4=}$ being such in these solids that the following thermodynamic equilibrium is reached:

isobutene $H^+ \rightarrow$ isobutene, *cis/trans*-but-2-ene and but-1-ene.

It appears from Table 2 that SAPO-11 has a larger number of external acid sites than Zr-SAPO-11.

Since it is known that these external acid sites are not selective for *n*-butene isomerization into isobutene,¹⁴ this suggests that part of the improvement in the initial isobutene selectivity for Zr-SAPO-11 may be due to this phenomenon. It is not known if this decrease in the number of acid sites for Zr-SAPO-11 is due to a preferential location of silicon inside the micropores or if the external acid sites are covered by ZrO_x entities.

Discussion

As shown by the XRD spectra, the two solids under study, SAPO-11 and Zr-SAPO-11, exhibit the AEL structure, and do not show any contamination by other crystallized phases. Scanning electron microscopy results do not indicate large differences between the morphologies of the two solids but it appears that the sizes of the Zr-SAPO grains are somewhat smaller than those of the SAPO-11.

Characterization of the acidity, either by using IR spectroscopy and/or by using ammonia TPD does not show large modifications due to the addition of zirconium: the number of acid sites, as evidenced by the IR vibration at 3630 cm^{-1} and by the second ammonia TPD peak, is smaller on Zr-SAPO than on SAPO-11.

Taking into account the results of elemental analysis and those obtained by NMR (70% of the Si in Zr-SAPO-11 create one proton), it can be calculated that the number of Brønsted acid sites in Zr-SAPO-11 is 70% of the number of Brønsted sites in SAPO-11, in good agreement with the IR and ammonia TPD results, which gave values of 60 and 50%, respectively.

Examination of the IR spectra and/or of the ammonia TPD results indicates that the presence of zirconium has not modified the acid strength of the acid sites of SAPO-11. These results, at this stage suggest that the zirconium is not incorporated in the framework of SAPO-11, at least in a significant manner, because we fail to detect any new type of acid center.

This finding suggests that zirconium may be deposited on the external surface of the zeolite particles and/or located inside the micropores of the material. The results obtained by measuring the pore volume through *n*-hexane absorption clearly indicate that for Zr-SAPO-11 the pore volume is reduced by an important factor since the pore volume of Zr-SAPO-11 is nearly 1/3 of that of SAPO-11. Since the XRD results indicate that both solids are highly crystalline, the decrease of the pore volume is probably due to partial pore blocking because of the presence of zirconium oxide inside the micropores.

The catalytic results, in particular the initial catalytic properties for *n*-butene isomerization, are in good agreement with such a picture; it has been shown recently¹⁰ that for medium pore zeolites or aluminophosphates, used for *n*-butene isomerization, there is a good correlation between the selectivity to isobutene and the pore diameter.

Therefore, the improved selectivity of Zr-SAPO-11 is attributed at least in part to the partial blocking of the pore by zirconium oxide.

Catalytic testing of 2,2,4-trimethylpentane cracking has shown that the number of acid sites located on the external surface of the individual crystals is much larger for SAPO-11 than for Zr-SAPO-11. Since it is known that these external sites are not selective for *n*-butene skeletal isomerization, the improved isobutene selectivity of Zr-SAPO-11 sample can be also attributed to this phenomenon.

It is observed that the stability with time on stream (TOS) is increased by the addition of zirconium: after 6 h on stream, SAPO-11 reacted with the same amount of reactant as the zirconium-based sample after 12 h, but the conversion is much less decreased on Zr-SAPO-11 catalyst.

Different factors may be at the origin of this improvement in stability with TOS. (1) A particle size effect. For a unidimensional pore system like SAPO-11, the size of the individual SAPO grains are of importance because it is very likely that the pore blockage, due to carbonaceous deposits, would be more severe for large grains compared to small grains. Examination of the SEM results indicates that the individual Zr-SAPO-11 grains are smaller than the SAPO-11 crystals. So, this could explain, at least partially, the better stability of the Zr-SAPO-11 catalyst. (2) Effect of external acid sites. Another factor which could influence the stability is the initial selectivity compared to SAPO-11, this having been attributed to higher pore constraints and to a lower number of external acid sites. Thus, the higher the selectivity, the lower the formation of butene oligomers which could be at the origin of the coke formation. Indeed, another important factor would be the lower number of external acid sites for Zr-SAPO-11 compared to SAPO-11: these external acid sites are probably at the origin of the ageing of the catalyst: formation of coke on the external surface of the grain would induce pore blockage and thus would decrease the activity of the catalyst. (3) A pore constraint effect. This effect will render the formation of carbonaceous deposits inside the pores more difficult, which will contribute to the ageing of the catalyst.

These three factors would explain the lower ageing rate of Zr-SAPO-11 compared to SAPO-11.

Conclusions

SAPO-11 and Zr-SAPO-11 have been synthesized. Characterization results indicate that zirconium is not incorporated into the SAPO framework but is localized, at least partially, in the pores of the solid, inducing a partial pore blockage. This partial pore blockage is at the origin of the increase in isobutene selectivity and is one of the causes of the improvement of catalyst stability with time on stream. In addition, a very small number of external acid sites of Zr-SAPO-11 as compared to SAPO-11 could also explain the improvement in isobutene selectivity and stability with time on stream.

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