Catalytic Activity of SAPO5 for Cracking of Butane and Hexane

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The catalytic properties of three SAPO5 samples for cracking of n-hexane and n-butane have been investigated. For characterization, both adsorption and temperature-programmed desorption of ammonia and pyridine were used. Only bridging hydroxyl groups (strong Brønsted-acid sites) were found to be active for both reactions. The catalytic activites of these sites were the same for all samples investigated. Differences exist with respect to the accessibility of n-butane and n-hexane. The variations of the turnover frequencies suggest that n-butane was converted over all Brønsted-acid sites present, whereas n-hexane was converted only over those sites that were able to adsorb pyridine. The product distribution and the apparent energies of activation suggest the prevalence of a monomolecular mechanism for cracking. As both molecules, n-butane and n-hexane, have nearly identical kinetic diameters, the transition state for n-hexane must be more bulky than that for n-butane.

Recently silicoaluminophosphate molecular sieves have attracted significant interest.¹⁻¹⁰ This interest was caused, on the one hand, by the large variety of new structures that could be synthesized^{3,4} and, on the other hand, by the widely varying strength and acid-site distributions which the material exhibits. Although some principal patterns of the variation of the acid-site distribution with structure and chemical composition are known, the level of understanding for SAPO5 is very limited compared to that for zeolites.

In comparison with ALPO molecular sieves, the introduction of silicon in SAPO molecular sieves leads to a significant increase in the concentration of catalytically active sites. The strength and concentration of the acid sites strictly depends upon the mode of the (formal) incorporation of silicon into the ALPO framework.^{3, 4, 6} Briefly, substitution of silicon for phosphorus should produce strong Brønsted-acid sites (and cation exchange capacity), substitution for aluminium should lead to the formation of strong basic sites (anion exchange capacity) and substitution for both aluminum and phosphorus should not change the acid-base (and the ion exchange) properties.

Because of the variety of possible concentrations of the framework constituents and the absence of detailed information on the local arrangement of cations at tetrahedral sites in the framework, some controversy exists about the acidity of these materials and the factors on which strength and concentration of the acid sites depend.⁷ In the following we intend to explore some of the causes of change of the catalytic properties with the variation of the composition of SAPO5 molecular sieves. We focus on SAPO5, not because the material is catalytically the most promising, but because up to now by far the most authors used ALPO5 and SAPO5 as material for their studies, thus providing invaluable reference.

Most of the studies^{3, 5, 6} classify SAPO5 as mildly acidic. Compared with ALPO5, SAPO5 was found to be *ca*. 300 times more active for the cracking of n-butane.³ However, no apparent correlation could be found between the K_A values measured and

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the concentration of silicon incorporated into the lattice or the intensity of i.r. bands of Brønsted-acidic hydroxyl groups.⁶ Moreover, Quinhua *et al.*⁶ found the catalytic activity for cumene cracking and *o*-xylene isomerization of SAPO5 to be comparable to that of HZSM5 at temperatures higher than 623 K. ALPO5 was found to be catalytically inactive for these reactions.

In a previous paper,¹⁰ we described the characterization of three SAPO5 samples with similar chemical compositions, but varying concentrations of silicon incorporated into the framework and hence with varying concentrations of acid sites and of amorphous impurities. We found that the i.r. spectrum of the activated samples shows four bands in the hydroxyl stretching region, which were attributed to SiOH groups (3745 cm^{-1}) , POH groups (3678 cm⁻¹) and bridged hydroxyl groups, which either point into the main (twelve-membered ring) channels (3626 cm^{-1}) or which are located in the six-ring units separating the main channels (3518 cm^{-1}) . The relative intensity of the band at 3745 cm⁻¹ increased with increasing concentration of the amorphous impurities. The concentration of strong Brønsted-acid sites, determined by temperature-programmed desorption (TPD) of ammonia, decreased in the same order. The acid strength was found to be considerably lower than that of the Brønsted-acid hydroxyl groups in highsilica zeolites and to be independent of the concentration of silicon incorporated into the lattice. This was concluded because of the identical temperature of the hightemperature desorption-rate maximum of ammonia during TPD and the similar wavenumber shifts of the band at 3626 cm⁻¹ after adsorption of benzene for all SAPO5 samples investigated.

In this communication we will focus on the catalytic properties of these SAPO5 samples for cracking of n-hexane and n-butane. Catalytic activity and selectivity will be described and discussed as a function of strength, concentration and accessibility of the Brønsted-acid sites.

Experimental

Synthesis

The synthesis procedure followed the description given in ref. (1). Pseudoboehmite and phosphoric acid were mixed intimately. SiO_2 was dissolved in an equimolar mixture of tetrapropylammonium hydroxide and tetraethylammonium hydroxide and the two mixtures were added together. The suspension was stirred for 15 min, placed in a steel autoclave and kept at 488 K for 24 h. Subsequently, it was filtered and the residue washed with distilled water. The solid was dried at 373 K for 12 h and was then calcined in air at 873 K for 1 h. Three SAPO5 samples and one ALPO5 sample were used for this study with compositions $Si_{0.140}$ $Al_{0.454}$ $P_{0.406}$ O_2 (SAPO5/1), $Si_{0.141}$ $Al_{0.442}$ $P_{0.417}$ O_2 (SAPO5/2), $Si_{0.152}$ $Al_{0.420}$ $P_{0.418}$ O_2 (SAPO5/3) and $Al_{0.5}$ $P_{0.5}$ O_2 (ALPO5).

I.R. Measurements

The samples were pressed into self-supporting discs with ca. 10⁸ N m⁻² compacting pressure and analysed by the infrared transmission-absorption technique. The disc was placed in a sample holder in the centre of a small furnace in the i.r. beam. The sample was heated with a rate of 10 K min⁻¹ to the temperature desired at pressures lower than 10^{-4} Pa. The i.r. spectra were recorded with a BRUKER IFS 88 FTIR spectrometer (4 cm⁻¹ resolution).

Temperature-programmed Desorption

TPD was carried out in vacuum (10^{-2} Pa) using a temperature increment of 10 K min⁻¹ between 400 and 1000 K. The reactor was a continuously pumped quartz glass tube,

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acid site (TPD maximum at)				
weak (513 K)	moderate (608 K)	strong (703 K)		
0.65	0.27	0.52		
0.50	0.19	0.68		
0.57	0.12	0.24		
0.39	0.33	0.00		
	acid site weak (513 K) 0.65 0.50 0.57 0.39	acid site (TPD maxi weak moderate (513 K) (608 K) 0.65 0.27 0.50 0.19 0.57 0.12 0.39 0.33		

Table 1. (a) Concentration of acid sites determined by TPD of pyridine per 100 Si_z Al_u P, O₂

Table 1. (b) Concentration of acid sites determined by TPD of ammonia per 100 Si_x Al_y $P_z O_2$

sample	acid site (TPD maximum at)				
	weak (460– 510 K)	moderate (540 K)	strong (580 K)		
SAPO5/1	0.69	0.45	0.98		
SAPO5/2	0.67	0.36	0.77		
SAPO5/3	0.54	0.25	0.38		
ALPO5	0.31	0.34	0.00		

connected to a Balzers 311 quadrupole mass spectrometer. The sample was calcined *in situ* at 873 K for 1 h, cooled to 300 K and contacted with 1500 Pa pyridine for 15 min. Then, prior to TPD, it was evacuated at 433, 493 and 553 K, in order to remove physisorbed, as well as weakly and moderately strong chemisorbed pyridine, respectively.

In order to quantify the amounts desorbed, the opening of the leak valve to the mass spectrometer and the amount of catalyst were kept constant during all experiments. The integrals of the rates of desorption were therefore proportional to the total amount of ammonia or pyridine desorbing from one adsorption state. By knowledge of the amount of tetrahedral aluminium, and hence the quantity of strong Brønsted-acid sites in a reference sample, the amounts of the desorbing gas in a given TPD maximum were quantified. These values are compiled in tables 1(a) and 1(b).

Cracking of n-Butane and n-Hexane

The reactions were carried out in a quartz glass tube of 30 cm length with an inner diameter of 0.4 cm. The temperature of the furnace and the flow rate were controlled electronically. The reaction mixtures were analysed by gas chromatography (HP5890A, equipped with a 50 m long Al_2O_3/KCl column and an FID). A six-port valve was used for the injection of the gas sample. For n-butane cracking, the feed contained 2 mol% n-butane in helium; for n-hexane cracking, the nitrogen stream was saturated with n-hexane at 291 K (14.7 mol%).

To activate the sample, it was heated in flowing helium up to 873 K and held at this temperature for a period of 30 min. The rates of reaction were measured between 733 and 813 K in intervals of 20 K. The conversion was kept below 5 mol% by variation of the space time. The data were analysed using the differential method.

Results

Adsorption and Desorption of Pyridine

As described in ref. (10) the i.r. spectrum of the activated sample of SAPO5 showed four bands of hydroxyl stretching vibrations at 3745, 3678, 3626 and 3518 cm⁻¹. These bands were attributed to SiOH,¹¹ POH¹² and two types of SiOHAl group,¹³ respectively.

The differences between the i.r. spectra of the activated samples and of the adsorbate with pyridine during equilibrium at 0.5 Pa are plotted as a function of exposure time in fig. 1(a) and (b). In such a plot, bands increasing in intensity upon the contact of the sample with pyridine point upwards, those decreasing point downwards. First, the terminal silanol groups and the P—OH groups, which gave rise to bands at 3745 and 3678 cm^{-1} , decreased in intensity. Also, with increasing exposure (1000 kL)† the intensities of the bands of the stretching vibrations of the strong Brønsted-acid hydroxyl groups at 3626 and 3518 cm⁻¹ decreased slightly. Simultaneously, the intensities of the bands of the C—H stretching vibrations at 3195, 3097, 3070 and 3035 cm⁻¹ increased. The bands of the 8a,b and 19a,b ring vibrations of pyridine were observed at 1635, 1610, 1591, 1577, 1547, 1489, 1448 and 1442 cm⁻¹. Except for the i.r. spectra recorded after the first 80 s of equilibration (which showed a higher relative intensity of the band at 1442 cm⁻¹) the intensities of all ring vibration bands increased simultaneously with increasing exposure.

The band at 1442 cm⁻¹ is characteristic of very weak Lewis-type interactions, presumably taking place at the outside of the SAPO crystallites. Because of the low relative intensity of the band at 1547 cm⁻¹ (characteristic of pyridinium ions¹⁴), we conclude that the major fraction of the adsorbed pyridine molecules was bound coordinatively. These pyridine molecules are adsorbed on two types of Lewis-acid sites, which in this case are most likely hydroxyl groups that are unable to protonate pyridine.

When the equilibrium pressure was increased in steps to 5, 50, 100 and 200 Pa, respectively, all bands due to adsorbed pyridine further increased in intensity (fig. 2). However, even after equilibration at 200 Pa (see fig. 2) the bands of the hydroxyl vibrations at 3745, 3678 and 3626 cm⁻¹ did not disappear completely. Thus, a significant fraction of the strongly acidic hydroxyl groups (3626 cm^{-1}) did not interact with pyridine. Since nearly all bands of the weakly acidic SiOH groups (3745 cm^{-1}) disappeared, we conclude that the inaccessibility of a part of the strong Brønsted-acid sites causes the incomplete coverage.

A series of i.r. spectra recorded during the desorption of pyridine is plotted in fig. 3. Upon evacuation at ambient temperature, the relative intensity of the band at 1448 cm⁻¹ decreased (in parallel with an increase of the intensity of the OH band at 3745 cm⁻¹). This suggests that the band at 1448 cm⁻¹ is indicative of pyridine adsorbed on SiOH groups, which agrees with previous results.¹⁵ Consequently, the band at 1442 cm⁻¹ must be attributed to pyridine adsorbed on POH groups. During TPD up to 573 K, the bands at 1610, 1591, 1448 and 1442 cm⁻¹ decreased in intensity. The bands at 1547 and at 1454 cm⁻¹ remained unchanged. Note that the band at 1454 cm⁻¹ was hardly visible as a shoulder after evacuation at ambient temperature. Above 573 K both bands decreased in intensity. The band at 1454 cm⁻¹.

The corresponding rates of desorption of strongly adsorbed pyridine during TPD (*i.e.* after evacuating the adsorbate at 423 K for 30 min) showed three maxima at 513, 608, and at 703 K (fig. 4.). This suggests the presence of three adsorption states (more precisely, three adsorption states during the TPD). By comparison with the relative changes of the i.r. spectra, the fraction of pyridine desorbed in the maximum at the

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Fig. 1. (a) I.r. spectra during adsorption of pyridine on SAPO5/1 at 0.5 Pa, between 3800 and 2800 cm⁻¹. The background of the activated sample was subtracted from each i.r. spectrum. The difference in time between the i.r. spectra is 60 s. (b) I.r. spectra during adsorption of pyridine on SAPO5/1 at 0.5 Pa, between 1800 and 1400 cm⁻¹. The background of the activated sample was subtracted from each i.r. spectrum. The difference in time between the i.r. spectrum. The difference in time between the i.r. spectrum.

highest temperature (703 K) was linked to the desorption from strong Brønsted-acid sites, which are characterized by i.r. bands at 3626 and 3518 cm⁻¹. We conclude that these sites are caused by substitution of phosphorus by silicon in the ALPO5 structure and since the maximum of the rate of desorption of pyridine from strong Brønsted-acid sites of HZSM5 was found at 854 K, the activation energy of desorption is somewhat lower for the investigated samples than for HZSM5 and hence the strength of the Brønsted-acid sites is also lower.

The TPD of pyridine from ALPO5 led to two maxima of the desorption rate at 513 and 608 K, indicating the absence of the strong acid sites in ALPO5. It suggests that the two maxima found at 513 and 608 K with both ALPO5 and SAPO5 are not necessarily related to the presence of silicon. From the comparison with the i.r. spectra recorded simultaneously, we concluded that desorption of pyridine from both silanol and POH groups gives rise to the maximum in the desorption rate at 513 K; the maximum at 608 K is due to desorption of pyridine from POH groups.

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Fig. 2. I.r. spectra during adsorption of pyridine on SAPO5/1 at 0.5, 5, 50, 100 and 200 Pa.



Fig. 3. I.r. spectra during TPD of pyridine from SAPO5/1, between 1800 and 1400 cm⁻¹. The background of the activated sample at ambient temperature was subtracted from each spectrum.



Fig. 4. Rates of desorption of pyridine during TPD after outgassing at 423, 493 and 553 K. (a) SAPO5/1, (b) SAPO5/2, (c) SAPO5/3, (d) ALPO5.

strong	Brønsted-acid sites,	obtained by TPD pyridine	of ammonia or
	cat. activity	/ TOF(amm.)/	TOF(py.)/
	mol g ⁻¹ s ⁻¹	(H ⁺) ⁻¹ s ⁻¹	(H ⁺) ⁻¹ s ⁻¹

 Table 2. Catalytic activities and turnover frequencies of cracking of n-butane, measured at 773 K and related to the number of strong Brønsted-acid sites, obtained by TPD of ammonia or pyridine

$mol g^{-1} s^{-1}$		$(H^+)^{-1} s^{-1}$	$(H^+)^{-1} s^{-1}$	
SAPO5/1	7.8 × 10 ⁻⁹	4.8×10^{-5}	9.1×10^{-5}	
SAPO5/2	$7.4 imes 10^{-9}$	5.9×10^{-5}	$6.7 imes 10^{-5}$	
SAPO5/3	3.9×10^{-9}	5.4×10^{-5}	$8.5 imes 10^{-5}$	
HZSM5	1.3×10^{-7}	$7.6 imes 10^{-4}$	7.6×10^{-4}	
	1.5 × 10	/.0×10	7.0 × 10	

Cracking of n-Butane

The reaction was carried out between 733 and 813 K (conversions below 5 mol %). The amount of products formed by thermal cracking was negligible in the range of temperatures used.¹⁶ The catalytic activities and turnover frequencies of the SAPO5 samples and of HZSM5 are compiled in table 2 (reference temperature: 773 K). Two

	product distribution (mol%) of SAPO5/1				
	733 K	753 K	773 K	793 K	813 K
methane	20.6	21.9	23.6	24.4	26.0
ethane	8.6	10.3	10.7	11.0	11.1
ethene	16.0	16.8	17.9	19.6	20.9
propane		1.2	0.9	0.9	0.8
propene	19.9	20.6	21.9	23.0	23.8
isobutane		0.9	0.7	0.6	0.4
E-but-2-ene	10.1	8.0	6.5	5.4	4.3
but-1-ene	7.7	6.5	5.3	4.5	3.4
isobutene	9.5	8.0	7.8	6.7	5.9
Z-but-2-ene	7.6	5.8	4.7	3.9	3.4

Table 3. Cracking of n-butane

Table 4. Cracking of n-hexane. Catalytic activities and turnoverfrequencies, measured at 773 K and related to the number ofstrong Brønsted-acid sites, obtained by TPD of ammonia orpyridine

	cat. activity/ mol $g^{-1} s^{-1}$	TOF(amm.)/ (H ⁺) ⁻¹ s ⁻¹	TOF(py.)/ (H ⁺) ⁻¹ s ⁻¹	
SAPO5/1	1.6×10^{-7}	9.9×10^{-4}	1.9 × 10 ⁻³	
SAPO5/2	1.0×10^{-7}	1.6×10^{-3}	1.8×10^{-3}	
SAPO5/3	8.2×10^{-8}	1.3×10^{-3}	2.1×10^{-3}	
HZSM5	$6.0 imes 10^{-6}$	3.6×10^{-2}	3.6×10^{-2}	

groups of values for the turnover frequencies were obtained using the concentrations of strong Brønsted-acid sites quantified either by TPD of ammonia or by TPD of pyridine. Since these two values differ from each other, the resulting turnover frequencies (TOF) are also different. Whereas similar turnover frequencies were obtained for all SAPO5 samples, HZSM5 showed a tenfold higher value of the turnover frequency for cracking of n-butane than SAPO5. Note that the variations between the turnover frequencies calculated were ± 6 % on the basis of TPD of ammonia and ± 15 % on the basis of TPD of pyridine. ALPO5 was inactive for cracking of n-butane. A typical product distribution is shown in table 3. The activation energies for the cracking of n-butane on SAPO5 were found to be in the range 142–163 kJ mol⁻¹.

Cracking of n-Hexane

The reaction was carried out between 733 and 813 K (conversions below 5 mol%). In contrast to cracking of n-butane, thermal cracking could not be neglected for cracking of n-hexane at temperatures higher than 753 K. For this reason the amount of products formed by thermal cracking (evaluated by measuring the conversion of n-hexane over quartz wool) was subtracted for every temperature and space velocity.

Table 4 shows the catalytic activities and the turnover frequencies of the SAPO5 samples for cracking of n-hexane, measured at 773 K. ALPO5 was at least three orders of magnitude less active. As for n-butane cracking, we related the activity at 773 K to

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	product distribution (mol%) of SAPO5/1				
	733 K	753 K	773 K	793 K	813 K
methane	11.9	12.9	12.5	11.9	11.4
ethane	10.4	11.1	11.3	10.9	10.7
ethene	1.3	1.3	1.2	1.2	1.3
propane	11.6	11.3	11.1	10.8	10.8
propene	46.4	44.5	43.1	44.7	45.6
butanes	4.4	4.5	4.7	4.8	4.7
butenes	10.7	10.2	10.9	10.2	10.8
pentanes	0.0	0.4	0.7	1.6	1.3
pentenes	3.3	3.8	4.5	3.9	3.4

Table 5. Cracking of n-hexane

the concentration of strong Brønsted-acid sites determined by TPD of ammonia and pyridine. In contrast to cracking of n-butane, the turnover frequencies were closer $(\pm 8\%)$ if the concentration was determined by pyridine TPD than if TPD of ammonia was used for the quantification of the acid sites $(\pm 23\%)$ (see table 4). Product distributions obtained after cracking of n-hexane over SAPO5/1 are compiled for various temperatures in table 5. The activation energies were all between values of 125 and 146 kJ mol⁻¹.

Discussion

Acid Sites and their Accessibility for Reactants

As has already been described in a previous publication,¹⁰ four different types of hydroxyl groups are present in SAPO5, *i.e.* silanol groups, POH groups and two types of bridged hydroxyl groups which are either located in the twelve ring channels or which point into the six ring units. TPD of ammonia shows the presence of weak, moderate and strong acid sites characterized by maxima of the rate of desorption at 460–510, 540 and 580 K [tables 1 (*a*) and (*b*)]. After comparison with the i.r. spectra recorded during TPD,¹⁰ the two maxima of the desorption rate at lower temperatures were attributed to the desorption of ammonia from SiOH and POH groups, and the maximum at 580 K to the desorption of ammonia from bridged hydroxyl groups. The acidity of these strong Brønsted-acid sites was found to be lower than in high silica zeolites and did not depend on the concentration of silicon incorporated into the lattice.¹⁰ With ALPO5, only sites of weak and moderate acid strength were found in consensus with the literature.^{17,18} Furthermore, at pressures higher than 0.5 Pa the adsorbate spectra of the SAPO5 samples with ammonia showed a complete coverage of the catalyst surface indicating that all acid sites were accessible for ammonia.

In contrast to ammonia, at low equilibrium pressures pyridine is primarily adsorbed on SiOH and POH groups, which terminate the lattice or which are part of the amorphous material in the pores. As these sites exhibit a much weaker acid strength than the bridging hydroxyl groups, the main fraction of pyridine is bound by weak, Lewistype, interactions. This preferential interaction of pyridine with sites which are located on the outer surface of the crystallites, irrespective of their acid strength, suggests the presence of significant diffusional limitations. Even equilibration with 200 Pa pyridine does not lead to a complete coverage of all hydroxyl groups of SAPO5/1, as can be seen in fig. 2. Thus, we conclude that a fraction of the strong Brønsted-acid sites located in the six-ring and twelve-ring channels are not accessible for pyridine. We suggest that this

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is due to the presence of amorphous impurities present in the pores, which lead to a narrowing of the effective pore diameter.

During TPD of pyridine three maxima of the desorption rate are observed at 513, 608 and 703 K (fig. 4), attributed to the desorption of pyridine from weak, moderate and strong acid sites. The higher temperatures of the three maxima of the desorption rate in comparison with the values obtained from the TPD of ammonia are explained by the higher strength of interaction between the adsorbent and the surface of the molecular sieve. For all SAPO5 samples, the concentrations of strong Brønsted acid sites obtained by TPD of pyridine are considerably lower than those obtained by TPD of ammonia [tables 1(a) and (b)]. For HZSM5, the concentration of the acid sites determined with both probe molecules gave identical values for the strong Brønsted acid sites and very similar values for moderately strong and weak acid sites. This confirms our conclusions drawn from i.r. measurements that a significant fraction of (Brønsted) acid sites is not accessible for pyridine.

Catalytic Activity for Cracking of n-Hexane and n-Butane

For cracking of n-butane and n-hexane, the catalytic activity generally decreases from SAPO5/1 to SAPO5/3 (tables 2 and 4). This can be explained by a decrease of the concentration of catalytically active sites in the same sequence. Analysing the data in more detail, however, reveals that subtle, but significant differences exist between n-butane and n-hexane, which will be discussed in detail below.

It is well accepted that the catalytic activity per acid site for cracking of n-hexane is at least three orders of magnitude higher for the strong Brønsted-acid sites (bridging hydroxyls) than for any other acid site [e.g. ref. (19)]. This explains the much lower activity of ALPO5 in comparison with the SAPO5 examples. Nevertheless, published results indicate that variations in the acid strength of the bridging hydroxyl group, *i.e.* the strong Brønsted-acid sites, may influence the catalytic activity and the product distribution in a less dramatic but significant way.²⁰⁻²²

For cracking of n-butane, calculation of the catalytic activity per strong acid site (quantified by the amount of ammonia desorbing in the maximum of the desorption rate at 580 K) leads to similar values of the turnover frequencies for all SAPO5 samples. This suggests that the acid strength of the catalytically active sites does not depend on their concentration in the material, being in good agreement with previous results.¹⁰ The higher acid strength of the strong Brønsted-acid sites in HZSM5, which had already been shown by TPD data, is also reflected in the tenfold higher value of the turnover frequency for cracking of n-butane (table 2).

For cracking of n-hexane the correlation between the concentration of strong Brønsted acid sites (quantified by TPD of ammonia) and the catalytic activity of the SAPO5 samples (table 4) is less significant. The turnover frequencies vary by $\pm 23\%$. Since the acid strength of the strong Brønsted-acid sites should be considered as constant for all SAPO5 samples, it was concluded that only a part of the sites which are active for cracking of n-butane are accessible for the n-hexane molecule. This indicates a bulkier transition state of n-hexane than of n-butane during the reaction pathway. The view of the restricted space around some acid sites has some support from the limited accessibility of the strong Brønsted-acid sites by pyridine. It is a remarkable coincidence that constant turnover frequencies of cracking of n-hexane ($\pm 8\%$) are obtained, if the concentration of strongly adsorbed pyridine molecules was used as the basis for calculation. This suggests that only those strong acid sites which are accessible for pyridine are actively participating in the cracking of n-hexane. All strong Brønsted-acid sites seem to participate in the cracking of n-butane.

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Selectivity for Cracking of n-Butane and n-Hexane

Cracking splits the butane molecule either into two C_2 -compounds or into methane and a C_3 -compound. Approximately equal amounts of methane and propene, but more ethene than ethane, were observed (see table 3). As to be expected by this scheme, only low concentrations of propane were found in the products. The higher concentrations of ethene than ethane are attributed to cracking of butenes (formed from n-butane by means of dehydrogenation). If these reactions proceed *via* a carbonium-ion mechanism, C—C bonds in the α position to the carbon atom bearing the positive charge have to be broken. This is characteristic for a monomolecular mechanism involving strong Brønsted-acid sites.^{20, 22, 23} Indeed, the reaction conditions employed in this study, *i.e.* high reaction temperature, low concentration of the reactant and low conversions, favour the monomolecular mechanism.²² The possibility of a radical mechanism for cracking has been disregarded, because of the strict proportionality of the catalytic activity and the concentration of strong Brønsted-acid sites. As the product selectivities did not vary significantly with increasing temperature, we conclude that similar energies of activation exist for the cleavage of all three carbon–carbon bonds of butane.

For cracking of n-hexane on SAPO5, high selectivities to methane and C₂-compounds were observed (table 5). In part, we assign this to the prevalence of a monomolecular mechanism²³ which proceeds via the formation of a pentacoordinated carbonium ion intermediate. The intermediate decomposes either by abstraction of hydrogen or by abstraction of an alkane^{22, 23} and the formation of a classical carbenium ion. In contrast, cracking of n-hexane by a bimolecular mechanism (via formation of a tricoordinated carbenium ion and cleavage of a C-C bond in the β position) leads primarily to the formation of propane and propene and low concentrations of methane and C₂ compounds.²⁴⁻²⁶ However, we conclude that part of the methane is produced by means of secondary cracking. We attribute the significant concentration of products formed by means of secondary cracking to the presence of amorphous material in the pores and the high reactivity of unsaturated hydrocarbons larger than propene formed during primary cracking. This explains the low selectivity for the formation of unsaturated C_5 molecules. We suggest that the presence of a higher concentration of propene than propane should be explained by cracking of hexene (possibly formed by dehydrogenation of n-hexane) and secondary cracking.

Conclusions

Evidence is presented that the catalytic activity of SAPO5 molecular sieves can be understood in terms similar to the catalytic activity of silica-alumina materials. The catalytic activity was found to depend strictly upon the concentration of the strongest Brønsted-acid sites. These sites could be identified as SiOHAl groups. Their strength was lower than that of high-silica zeolites and similar to that of faujasites. This agrees well with recent experiments reported by Lechert and co-workers²⁷ for the transformation of aromatic compounds. The strength of the acid sites hardly varied for the series of samples we investigated. Subtle differences have been noted between the cracking of n-hexane and that of n-butane which suggest that the method of determination of the concentration of acid sites, *i.e.* ammonia *vs.* pyridine TPD, is extremely important in understanding quantitatively the variations in the catalytic properties.

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