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Infrared Study of Cyclohexanol Chemisorption in SAPO Molecular Sieves

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The infrared spectra of cyclohexanol adsorbed on SAPO molecular sieves (four SAPO-5 samples with different SiO_2 contents, SAPO-11 and SAPO-31 were studied) show bands due to cyclohexanone (1732 cm^{-1}) at room temperature, while on heating cyclohexene is formed. The results are discussed in terms of the existence of basic sites parallel to the Brønsted acid sites.

The catalytic activity of molecular sieves is related to the existence of active sites. The similarity of their framework composition and microporous structure with those of zeolites prompted investigations into the catalytic activity of these materials in acid-catalysed reactions such as cracking,[1–4] isomerization[4] and alcohol conversion.[5,6] The parallel examination of the hydroxyl groups by IR spectroscopy permits the correlation between the Brønsted acidity and catalytic activity to be followed. It has been found that the characteristic bands for the hydroxyl groups in SAPO-5 (3745, 3678, 3629, 3520 cm^{-1}) are the same for SAPO-11,[1] although SAPO-5 exhibits strong acidity and SAPO-11, weak to mild acidity. In SAPO-31 the bands at 3742, 3675, 3620 and 3520 cm^{-1} correspond to Si—OH, P—OH and two types of bridging OH groups, respectively. Only the bridging OH groups in SAPO-5 are active for cracking.[2] The strength of the Brønsted acid sites in SAPO-5 is lower than that for high-silica zeolites and similar to that for faujasites.

Recently, we have found that sites with dehydrogenation activity exist simultaneously with the Brønsted acid sites in HZSM-5 zeolites.[7] These sites might be anions, such as O^{2-}, AlO_4^- or OH^-. Taking into account the differences in the pore dimensions of SAPO molecular sieves:[8]

SAPO-5	12-membered ring	0.73 nm
SAPO-11	10-membered ring (elliptic)	0.39; 0.63 nm
SAPO-31	10-membered ring	0.71 nm

we attempted to compare their behaviour towards cyclohexanol using IR spectroscopy.

Experimental

Materials

The compositions of the gels used for the synthesis of the molecular sieves investigated are presented in Table 1. The crystallization was performed at 443 K over 72 h. The crystallinity of the products was determined by X-ray diffraction.

Table 1 Molar oxide ratios in the synthesis of SAPO molecular sieves

molecular sieve		Al_2O_3	P_2O_5	n-Pr_3N	SiO_2	H_2O
SAPO-5	0.1 SiO_2	1	1	1	0.1	30
	0.2 SiO_2	1	1	1	0.2	30
	0.3 SiO_2	1	1	1	0.3	30
	0.4 SiO_2	1	1	1	0.4	30
SAPO-11	0.3 SiO_2	1	1	0.6[a]	0.3	30
SAPO-31	0.3 SiO_2	1	1	1[a]	0.3	30

[a] n-Pr_2NH.

Cs SAPO-5 (0.1 SiO_2) was prepared by a three-fold treatment of the molecular sieve with a 0.1 mol dm^{-3} solution of caesium nitrate at 363 K.

Techniques

IR spectra were recorded at the temperature of the IR beam using a Perkin-Elmer 983 G spectrophotometer. The samples were pressed into self-supporting wafers (diameter 14 mm, weight 15–20 mg), heated for 4 h at 723 K under air and then evacuated to 1.3×10^{-2} Pa for 6 h at the same temperature.

Reagent-grade alcohol vapours were introduced at ambient temperature after a freeze–pump–thaw cycle. The spectra were recorded after heating the adsorbent in contact with the alcohol at different temperatures.

Results and Discussion

A band at 1732 cm^{-1} appeared immediately after contact of cyclohexanol with the SAPO molecular sieves. Under the same conditions AlPO-5 does not show any activity towards cyclopentanol, in agreement with the results in ref. 9, where only very weak base sites, moderately strong Lewis acid sites and weak Brønsted acid sites have been found in microporous $AlPO_4$.

Fig. 1 shows the variation of the intensity of the band at 1732 cm^{-1} with the temperature of contact. The decrease of the intensity caused by heating was accompanied by the appearance at 373 K of bands at 3045 and 1655 cm^{-1}. The first is characteristic of a $\nu_{=C-H}$ vibration, while the second is related to the vibrations of water molecules. Both of these increased on further heating. Evidently, dehydration of the alcohol had occurred.

Using literature data[9] for the free energy, we calculated rate constants for dehydration and dehydrogenation of cyclohexanol at different pressures (Table 2). It is evident that dehydration is the main reaction. Dehydrogenation is favoured by reduced pressure, as was observed in our experiments.

Table 2 Calculated rate constants[a]

	$p = 1$ atm.		$p = 10^{-7}$ atm.	
T/K	cyclohexene	cyclohexanone	cyclohexene	cyclohexanone
300	4.9	1.4	5.4	2.1
400	68.5	7.2	64.3	13.7
500	120.0	52.0	118.0	71.0

[a] Ref. 10.

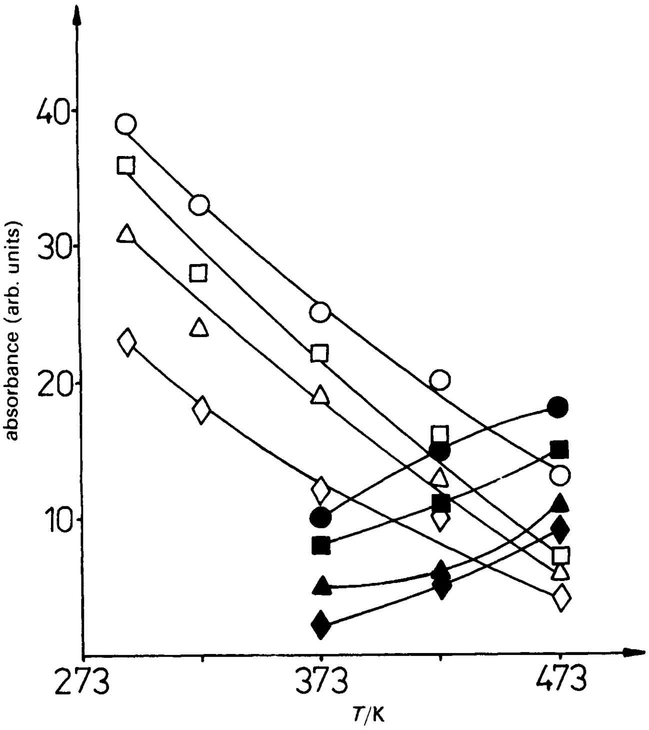

Fig. 1 Temperature dependence of the intensities of the bands at 1732 cm^{-1} (open symbols) and 1655 cm^{-1} (filled symbols) resulting from contact of SAPO-5 with cyclohexanol: (◇, ◆) 0.1; (△, ▲) 0.2; (□, ■) 0.3; (○, ●) 0.4 SiO_2

In addition to the Brønsted acid sites, hydrogen-accepting sites, probably of basic character, also exist in SAPO molecular sieves, similar to the case for H-ZSM-5 zeolite. The numbers of both types of active site increase for higher SiO_2 contents in the crystal framework (Fig. 1). This corresponds to the generation of SAPO-type Brønsted acid sites, as proposed in ref. 3.

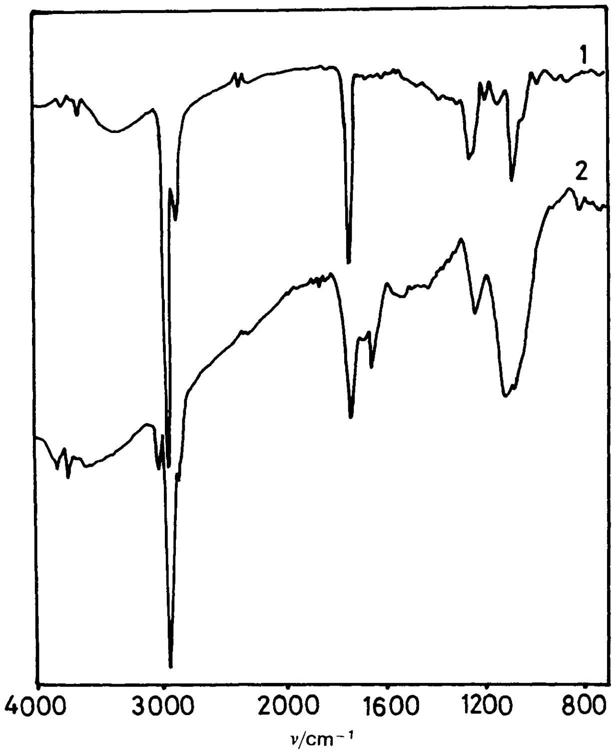

Fig. 2 IR spectra of cyclohexanol adsorbed at 423 K on Cs-SAPO-5 (0.1 SiO_2) (1) and SAPO-5 (0.1 SiO_2) (2)

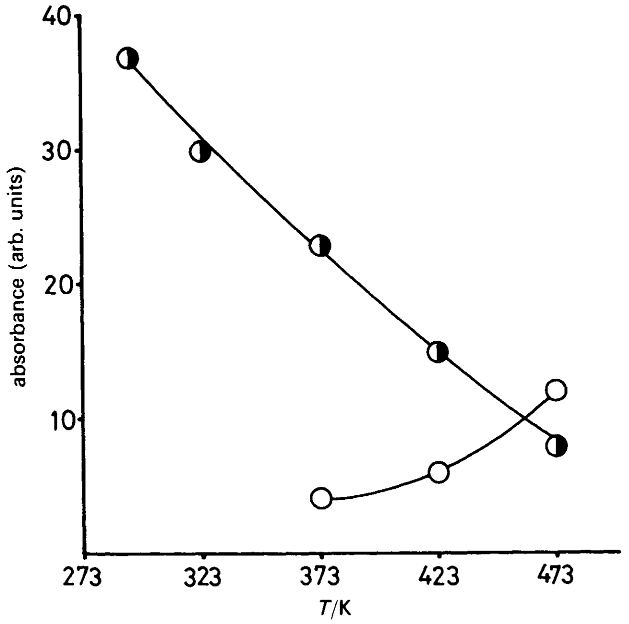

Fig. 3 Temperature dependence of the intensities of the bands at 1732 cm^{-1} (◑) and 1655 cm^{-1} (○) due to cyclohexanol chemisorbed on SAPO-11

The basic nature of the dehydrogenation sites was confirmed by the experiment with Cs-SAPO-5 (Fig. 2). Only a band at 1732 cm^{-1}, characteristic of the formation of cyclohexanone from cyclohexanol, was observed up to 473 K. The bands for cyclohexene (3045 and 1655 cm^{-1}) were absent. The amount of the carbonyl compound was greater than in the presence of the H-form of the molecular sieve. As in the case with ZSM-5 zeolites, the basicity depends on the counter-cation. Similar active sites exist on SAPO-5, SAPO-11 and SAPO-31 (see Fig. 3 and 4). Among the molecular sieves investigated, the most active for dehydration and dehydrogenation of cyclohexanol is SAPO-5 (0.4 SiO_2).

The basic sites may be oxygen atoms from the framework in different environments, *e.g.* Al—O—P, Si—O—Si or Si—O—Al.[1] It is difficult to distinguish between these three

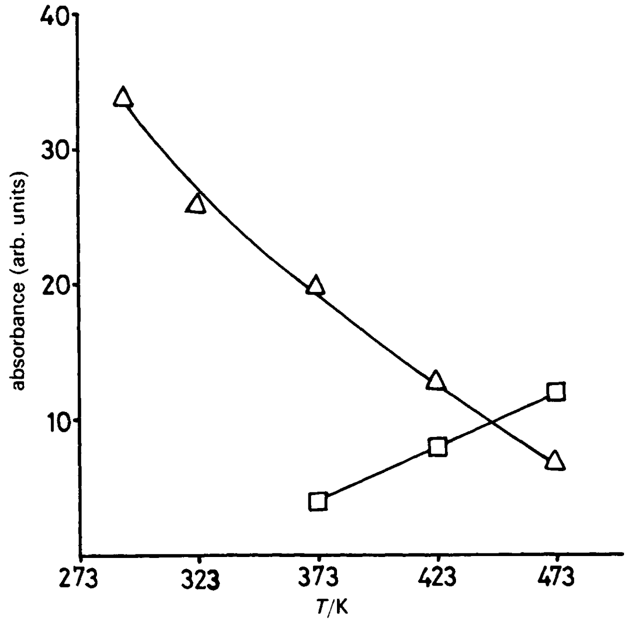

Fig. 4 Temperature dependence of the bands at 1732 cm^{-1} (△) and 1655 cm^{-1} (□) due to cyclohexanol chemisorbed on SAPO-31

types of site. The relation reported in ref. 7, that the concentration of Brønsted acid sites, as well as of basic sites, is proportional to the aluminium content, allows the Si—O—Si sites to be eliminated. The lack of activity of AlPO-5 enables us to reject Al—O—P as the active basic site. According to the observed activity for cracking,[2] the site for the formation of bridging OH groups must be basic. So the basic sites on SAPO molecular sieves must be the oxygens in Si—O—Al.

Conclusions

The molecular sieves SAPO-5, SAPO-11 and SAPO-31 may activate not only the dehydration but also the dehydrogenation of cyclohexanol. The dehydration activity is related to the existence of Brønsted acid sites, while the dehydrogenation provides evidence for the presence of hydrogen-accepting sites, probably of basic character. Both types of active site are related to the Si—O—Al groups.

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