COMPARISON OF HZSM-5 ZEOLITE AND SAPO-5 MOLECULAR SIEVE IN 1-HEXANOL CONVERSION*

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Received September 13, 1991
Accepted October 22, 1991

The IR spectra of 1-hexanol adsorbed on SAPO-5 molecular sieves and on HZSM-5 zeolite were compared. It has been found that both types of catalysts activate at 423 K the dehydration of 1-hexanol. In the IR spectra bands at 670 cm^{-1} (*Z*-isomer), 889 cm^{-1} ($CH_2{=}C{<}$ fragment), 911 cm^{-1} ($CH_2{=}CH{-}$) and 965 cm^{-1} (*E*-isomer) have been observed, indicating that the skeletal and positional isomerization took place. A carbonyl compound (1 730 cm^{-1}) was formed at room temperature on all the investigated catalysts and disappeared upon heating. The activity of HZSM-5 in olefin isomerization and in dehydrogenation was greater than that of SAPO-5.

The interest in the catalytic properties of silicoaluminophosphate (SAPO) molecular sieves is related to the variety of structural elements in the framework bonds as Al—O—P, Si—O—Al and Si—O—Si, that might generate active sites of different acid-base properties[1-7].

The similarity of their framework composition and microporous structure with that of zeolites directed the investigations on the catalytic activity of these materials in acid catalyzed reactions as cracking[2-5], isomerization[5] and alcohol conversion[6,7]. The parallel examination of the hydroxyl groups by IR spectroscopy permits the correlation between the Broensted acidity and catalytic activity to be followed. It has been found that the characteristic bands for the hydroxyl groups in SAPO-5 at 3 745, 3 678, 3 629, 3 520 cm^{-1} corresponded to Si—OH, P—OH and to two types of bridging OH groups, respectively. Only the bridging OH groups in SAPO-5 are active in cracking[3].

In a previous work we have found[8] that HZSM-5 zeolites with different Si/Al ratios activate dehydration of 1- and 2-butanol accompanied by isomerization of the olefin. Skeletal isomerization was observed on the zeolite with greatest concentration of Brønsted acid sites but some authors[9] suggest the participation of strongest sites

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* Presented as a poster at the *International Symposium "Zeolite Chemistry and Catalysis", Prague, September 8—13, 1991.*

in this reaction. The aim of our work was to compare the behaviour of 1-hexanol adsorbed on SAPO-5 molecular sieves with different contents of SiO_2 and on HZSM-5 zeolite using IR spectroscopy.

EXPERIMENTAL

Materials

ZSM-5 zeolite with Si/Al ratio of 50 has been synthesized. The H-form has been obtained after decomposition of the tetrapropylammonium bromide (TPA-Br) at 873 K and treatment with 0·6M hydrochloric acid at room temperature.

The composition of the gels used for the synthesis of the SAPO-5 molecular sieves investigated were: Al_2O_3; P_2O_5; n-Pr_3N; SiO_2 (0·1; 0·2; 0·3; 0·4); 30 H_2O.

The crystallinity of the products was monitored by X-ray diffraction, by scanning microscopy and by IR spectra in KBr. The particle-size distributions of the different samples did not vary appreciably. No experiments were done to detect different zones in the composition of the crystals.

Techniques

IR spectra were recorded at the temperature of the IR beam using Perkin Elmer 983G spectrophotometer. The samples were pressed into self-supporting wafers (diameter 14 mm, weight 15–20 mg), heated 4 h at 723 K under air and then evacuated to $1{\cdot}3 \,.\, 10^{-2}$ Pa for 6 h at the same temperature.

Reagent grade 1-hexanol vapours were introduced at ambient temperature after freeze-pump-thaw cycle. The spectra were recorded after heating the adsorbent in contact with the alcohol at different temperatures. The spectral resolution was 3 cm^{-1}.

RESULTS AND DISCUSSION

Recently we have shown, that 1- and 2-butanol may react with the acid as well as with basic sites of the HZSM-5 zeolites, giving the corresponding olefin, its isomers and a carbonyl compound[8,10]. The dehydrogenation was more pronounced using cyclohexanol[10].

Our IR studies of 1-hexanol adsorption on HZSM-5 zeolite and on SAPO-5 molecular sieves showed that at room temperature a carbonyl compound (1 730 cm^{-1}) was formed and disappeared upon heating. Probably it was decomposed into olefin, by analogy with the interaction of 2-propanol and NaZSM-5 (ref.[11]). The intensity of the band at 1 730 cm^{-1} on HZSM-5 zeolite was greater than that on SAPO-5.

After heating the system at 423 K in the IR-spectra of 1-hexanol adsorbed on HZSM-5 and on SAPO-5 the bands at 670, 889, 911, 965 and 990 cm^{-1} appeared, characteristic for alkenes[12] (Figs 1–3).

The bands at 911 and 990 cm^{-1} characterize the vinyl group ($CH_2{=}CH{-}$) (ref.[11]), whereas at 889, 965 and 670 cm^{-1} the end methylene group ($CH_2{=}C\langle$), *E*- and *Z*-olefin, respectively[12].

At 423 K the most intensive was the band at 965 cm^{-1}, characteristic for *E*-olefins. This result corresponds to the GC analysis of the products of 1-hexene isomerization on HZSM-5 zeolite[13]. Upon heating the concentration of *E*-isomer diminished. The intensities of the bands at 911 and 670 cm^{-1}, for 1-hexene and the *Z*-isomer, respectively, were relatively low. The most interesting was the band at 889 cm^{-1}, characteristic for $CH_2=C$ fragments in alkenes. Its presence in the IR spectra of

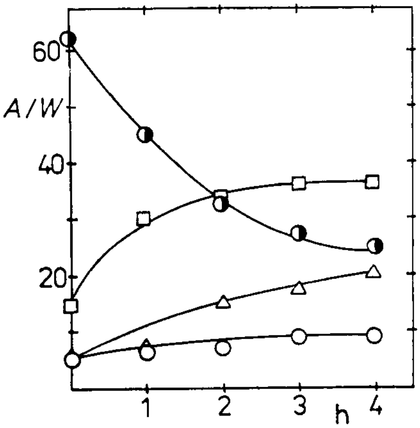

FIG. 1

Dependence of the intensity (*A*) of the bands per gram catalyst (*W*) on the contact time between 1-hexanol and HZSM-5 with Si/Al = 50 at 473 K (at zero contact time the values at 423 K are given) ○ 670 cm^{-1}, *Z* isomer; □ 889 cm^{-1}, $CH_2=C$; △ 911 cm^{-1}, $CH_2=CH—$; ◑ 965 cm^{-1}, *E* isomer

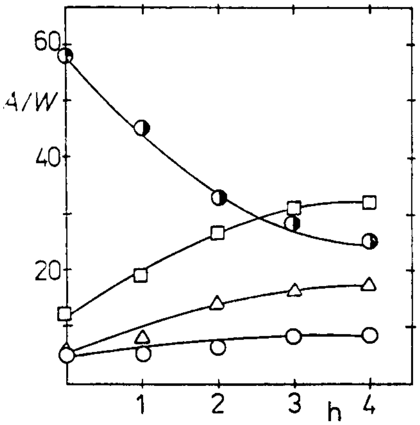

FIG. 2

Dependence of *A*/*W* on the contact time between 1-hexanol and SAPO-5 0·4 SiO_2 at 473 K (symbols as in Fig. 1)

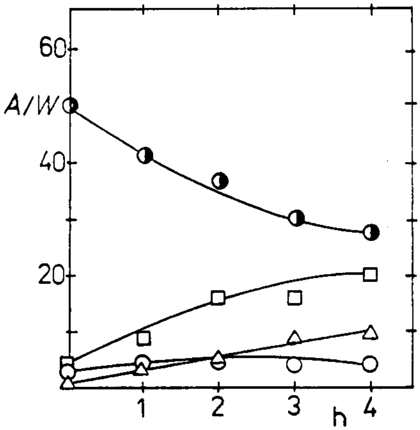

FIG. 3

Dependence of *A*/*W* on the contact time between 1-hexanol and SAPO-5 0·1 SiO_2 at 473 K (symbols as in Fig. 1) hexenes might be related to the existence of 2-methyl-1-pentene. This band increased its intensity upon heating and overlap that of the *E*-isomer on HZSM-5 and on SAPO-5 (0·4 SiO_2) e.g. on the zeolites with highest concentration of bridging

TABLE I
Calculated thermodynamic equilibrium ratio of some hexenes[14]

Compound	Temperature, K	
	400	500
1-Hexene	0·5	1·2
E-2-Hexene	12·3	14·2
Z-2-Hexene	15·2	18·4
2-Methyl-2-pentene	53·7	42·4
2-Methyl-1-pentene	9·5	14·6
E-3-Hexene	1·6	2·5
Z-3-Hexene	7·2	8·3

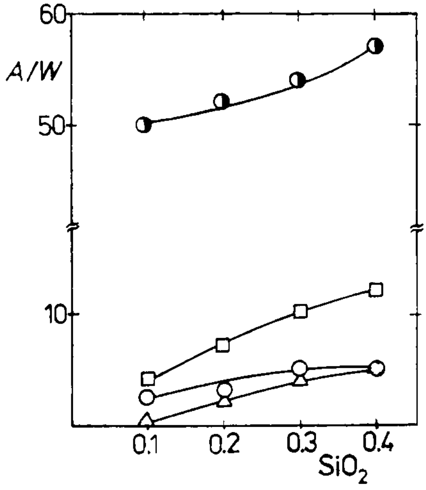

FIG. 4
Dependence of *A*/*W* as a function of the SiO_2 molar content after 1-hexanol adsorption at 423 K (symbols as in Fig. 1)

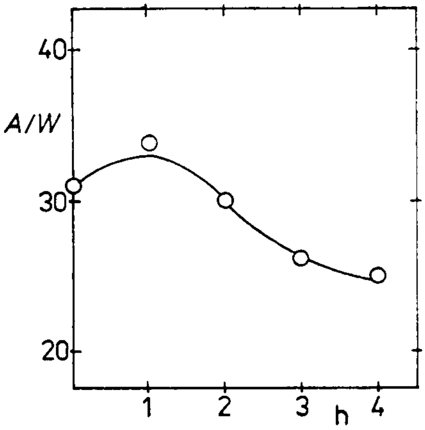

FIG. 5
Changes of intensity (*A*) of the band at 1 507 cm^{-1} on the disc per gram catalyst (*W*) with time (1-hexanol and SAPO-5 0·4 SiO_2) at 473 K

hydroxyl groups. The existence of the band, characteristic for 2-methyl-2-pentene (840 – 790 cm^{-1}) was absent. The comparison of these results with thermodynamic data on the ratio between some of the isomeric hexenes (Table I)[14] leads to the conclusion, that the thermodynamic equilibrium was not yet achieved, similar to the results in ref.[13].

Anyhow it permits a comparison between the HZSM-5 zeolites and SAPO-5 molecular sieves. The similarity of both types of solids is evident. The nearest to HZSM-5 is SAPO-5 with more SiO_2 (Figs 1 and 2), the comparison between the SAPO-5 samples investigated (Fig. 4) shows that the isomerization activity increases in parallel with the SiO_2 content, confirming its relation to the acidity[4].

The dependences between the isomerization activity and the acidity of the samples support the carbenium ion mechanism of alcohol dehydration and olefin isomerization. The band at 1 507 cm^{-1}, observed in the IR spectra of the adsorbed species on the catalysts studied at 423 K (Fig. 5) might be considered as a characteristic of the intermediates. The change of its intensity with the contact time corresponds to the interpretation of this band as a shifted double bond stretching, influenced by interaction with a proton and forming probably a π-complex[8].

In conclusion, the IR spectra of adsorbed alcohols are a convenient test for characterization of the acid sites on the surface of solids. Information is obtained for the nature of the reaction products, as well as on the nature of some intermediates. The similarities found in the behaviour of HZSM-5 zeolite and SAPO molecular sieves in 1-hexanol conversion correspond to the presence of bridging OH groups in both type of solids.

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