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IR study of cyclic alcohol adsorption on titanium containing zeolites

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The IR spectra of adsorbed cyclohexanol and cyclohexylmethanol were used to compare the catalytic properties of Ti-containing pentasils with that of Ti-silicalite (TS-1) and TiO_2 (anatase). While TiO_2 had basic character evidenced by alcohol dehydrogenation, TS-1 possessed also some weak acid sites able to dehydrate the alcohol. The acid properties were improved by the introduction of aluminum into the Ti-ZSM-5 samples.

Keywords: Ti-zeolites; TS-1; anatase; cyclohexanol; cyclohexylmethanol; IR spectra

1. Introduction

Different elements may be introduced beside Si and Al into several zeolite frameworks. From this procedure a variety of substances with interesting properties in adsorption and catalysis were obtained. Titanium containing molecular sieves received special interest in the last years [1].

Two main groups of Ti-containing zeolites might be distinguished. Ti-silicalites and crystalline Ti-aluminosilicates. The first type showed remarkable activities in the oxidation of organic compounds by H_2O_2 [2], while the others were active in acid catalyzed reactions [3]. Efforts were made to identify the nature of the active sites of these catalysts. It has been established [4] that the catalytic activity of TS-1 in phenol hydroxylation, 1-octene epoxidation and *n*-hexane oxygenation by aqueous H_2O_2 was related to the titanyl groups. The presence of two different titanium phases in TS-1 has been established [5]. Lewis and Brønsted acid sites were registered using pyridine adsorption [5]. The acidity of the samples influenced the selec-

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tivity of TS-1 catalysts. Pyridine chemisorption has been used for the characterization of acid site distribution in H/La/ETAS-10 (Engelhardt titanium aluminosilicate) [3]. According to refs. [4,6] the presence of small amounts of finely divided anatase may induce some basic properties.

Recently we have proposed the conversion of cyclohexanol as a test for the acid–base properties of some catalysts [7]. In the present study we used cyclohexanol and cyclohexylmethanol as probe molecules for the characterization of the active sites of some Ti-containing zeolites. Primary and secondary alcohols with similar molecular dimensions have been chosen in order to distinguish between the acid and base properties of the investigated catalysts.

2. Experimental

2.1. ZEOLITES

Three samples of TiNa-ZSM-5 have been synthesized from batches of the molar composition: SiO_2 0.0094$NaAlO_2$ 0.19NaOH 0.04TPABr (tetrapropylammonium bromide) $x$$TiOSO_4$ 10.4H_2O with $x = 0.013$ (1), 0.026 (2), 0.066 (3). The crystallinity of the samples checked by X-ray diffraction was (1) 100%, (2) 83%, and (3) 65%.

The corresponding H-forms were prepared after the template decomposition by heating to 873 K for 6 h under air flow, a treatment with 0.5 M NH_4Cl solution (40 ml per g zeolite) and calcination at 773 K.

The MFI (ZSM-5) structure has been confirmed by the IR spectra in KBr by the bands at 450, 549, 790, 1100 and 1220 cm^{-1}. The band at 960 cm^{-1}, characteristic for titanium in the zeolite lattice [8] appeared only as a shoulder. ZSM-5 ($Si/Al = 50$) was used in the H-form obtained by room temperature treatment of the template free zeolite with 0.6 M HCl solution (38.5 ml per g zeolite) for 24 h. Cs-ZSM-5 was prepared by threefold exchange with 0.1 M $CsNO_3$ solution. TS-1 was synthesized according to ref. [9] with $SiO_2/TiO_2 = 45$ corresponding to 2.8 wt% TiO_2. The band at 960 cm^{-1} was well presented in the IR spectra in KBr. TiO_2 (anatase, Merck p.a.) was used as a reference substance.

2.2. IR SPECTRAL PROCEDURE

Self-supporting wafers with 14 mm diameter and 15–30 mg weight were heated for 4 h at 723 K under air and then evacuated at the same temperature for 6 h at 1.3×10^{-2} Pa. Reagent grade alcohol vapors were introduced into the IR cell at room temperature after a freeze–pump–thaw cycle. The spectra were recorded using a Perkin Elmer 983 G spectrophotometer at room temperature after a contact time of 1 h with the alcohol vapors at different temperatures between 323 and

473 K. The spectra of the gas phase only were recorded by moving the wafer out of the beam. Assignments of the IR bands [10,11] are given in table 1.

3. Results

3.1. CYCLOHEXANOL ADSORPTION

In the IR spectra of cyclohexanol in contact with the Ti-containing zeolites we observed the appearance of the following new bands: 3030–3040, 1730–1705 and 1512 cm^{-1} (fig. 1). The intensity and the position of the bands varied in dependence on the temperature and the catalyst. The position of some bands was changed by the adsorption.

The temperatures at which the bands appeared in the presence of different catalysts are shown in table 2. All the investigated catalysts caused the formation of a carbonyl compound (cyclohexanone) at room temperature (band at 1730 cm^{-1}). In similar conditions we observed the same reaction in the presence of H-ZSM-5 zeolites [12,13]. By heating at higher temperature the acid forms of the catalysts caused the formation of alkene. This dehydration reaction was not observed in the presence of the Na-forms of the molecular sieves and TiO_2 which do not possess any Brønsted acid sites. The band at 1512 cm^{-1} appeared at 423 K only on the surface of TiH-ZSM-5 (1).

We followed the changes of the intensities of the carbonyl band of cyclohexanone and the alkene band of cyclohexene in dependence on the temperature. The carbonyl band diminished by heating (fig. 2).

TiH-ZSM-5 (2), a sample with higher Ti content and good crystallinity, was most active in carbonyl formation. The influence of Ti on the hydrogen accepting sites was evident from the activities of anatase and TS-1 in the same reaction (figs. 3, 4, 5). As in the case with ZSM-5 zeolites the dehydrogenation activity of

Table 1
Assignments of the IR bands

Band (cm^{-1})	Interpretation [9,10]
3030–3040	$=C-H$
2937	CH_3
2336	CO_2
2180	CO
2120	CO
1730–1705	$>C=O$
1512	$C=C$
1380	$\delta\ CH_3$
800	trisubstituted alkene
718	cyclohexene

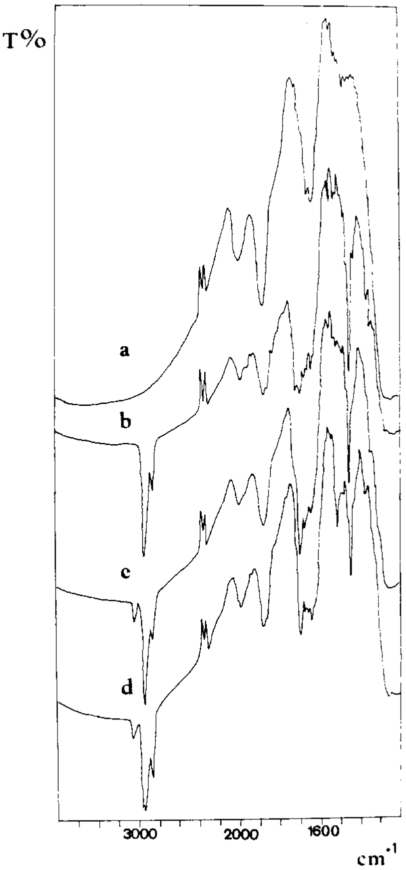

Fig. 1. IR spectra of (a) TiH-ZSM-5 (1) after evacuation at 723 K, 6 h; (b) adsorbed cyclohexanol at room temperature; (c) adsorbed cyclohexanol at 373 K; (d) adsorbed cyclohexanol at 473 K.

Table 2
Temperatures at which new bands appeared in the IR spectra of cyclohexanol interacting with the studied catalysts

Catalyst	1730 cm^{-1}	3030 cm^{-1}	2180, 2120, 2336 cm^{-1}	800 cm^{-1}
TiH-ZSM-5 (1)	293	323	–	473
TiH-ZSM-5 (2)	293	323	473	–
TiH-ZSM-5 (3)	293	373	–	473
TiNa-ZSM-5 (1)	293	–	–	–
TiNa-ZSM-5 (2)	293	–	–	–
TS-1	293	473	–	–
anatase	293	–	–	–

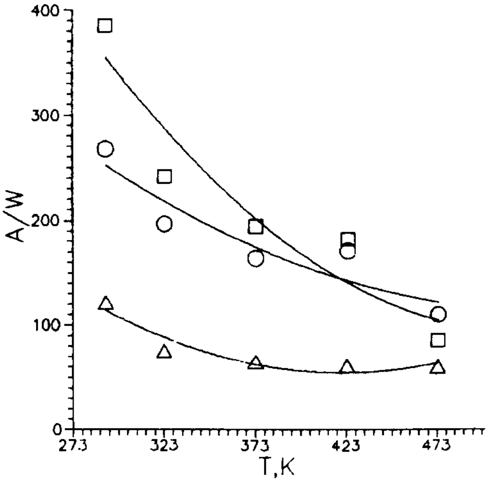

Fig. 2. Temperature dependence of A/W (A absorption at 1730 cm^{-1}; W weight of the zeolite sample) for cyclohexanol in interaction with TiH-ZSM-5: (1) (○), (2) (□), (3) (△).

the Ti-containing analogs depended on the nature of the counter cation. The forms containing alkali cations are more selective than the acid forms.

The carbonyl compound was found in the gas phase as well as adsorbed on the catalyst surface. In the adsorbed state the carbonyl band was shifted to 1705 cm^{-1}. The comparison of the carbonyl band intensity in the gas and for the adsorbed species (fig. 6) showed that an increasing amount of carbonyl was adsorbed heating from ambient temperature to 323 K. It remained almost constant up to 423 K and

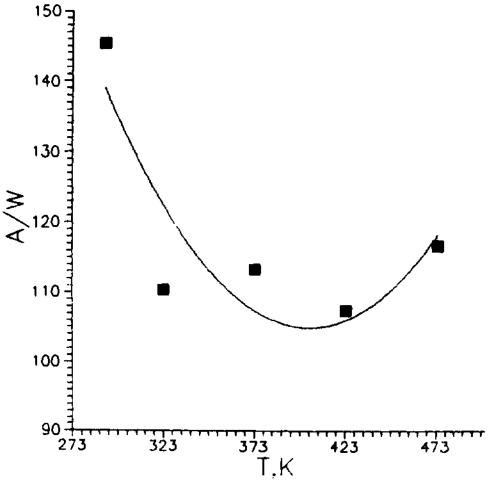

Fig. 3. Temperature dependence of A/W at 1730 cm^{-1} for cyclohexanol in interaction with anatase.

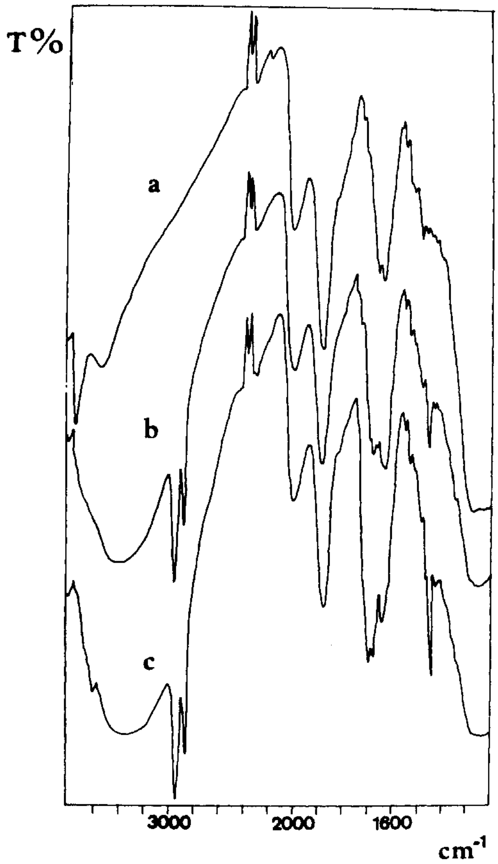

Fig. 4. IR spectra of TS-1: (a) evacuated at 723 K; (b) cyclohexanol adsorbed at room temperature; (c) cyclohexanol adsorbed at 323 K.

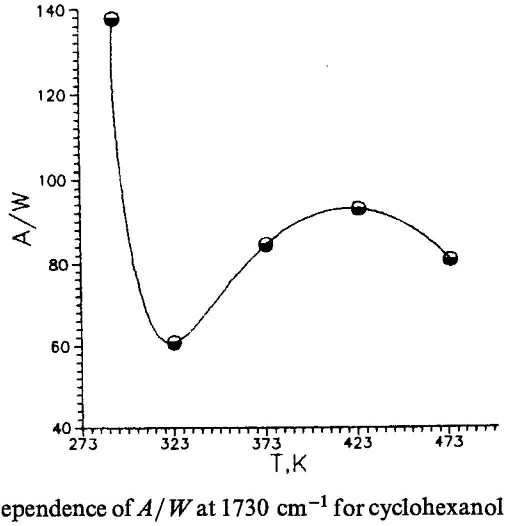

Fig. 5. Temperature dependence of A/W at 1730 cm^{-1} for cyclohexanol in interaction with TS-1.

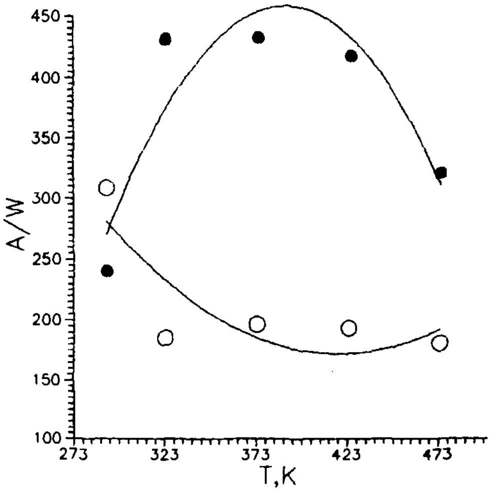

Fig. 6. Temperature dependence of A/W at 1730 cm^{-1} for cyclohexanol adsorbed on TiNa-ZSM-5 (2): (●) band at 1705 cm^{-1} of adsorbed species; (○) band at 1730 cm^{-1} for the gas.

then decreased. Corresponding to the increase in the adsorbed phase the gas phase showed a decrease of the carbonyl band.

The dehydration ability of Ti-containing pentasils (fig. 7) was highest in sample (1) which had the highest crystallinity. At 473 K both the carbonyl and the alkene quantities decrease and the bands of CO (2180, 2120 cm^{-1}) and CO_2 (2336 cm^{-1}) appeared indicating some destructive oxidation.

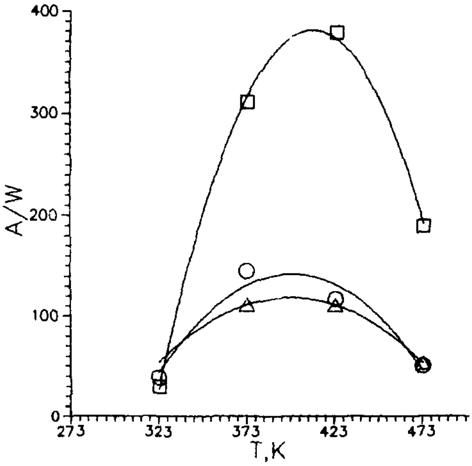

Fig. 7. Temperature dependence of A/W at 3030 cm^{-1} for cyclohexanol in interaction with TiH-ZSM-5: (1) (□), (2) (○), (3) (△).

In the presence of TiH-ZSM-5 (1) by heating to 473 K we observed the formation of doublets at 3030 and 2937 cm^{-1}. Simultaneously new bands at 800 and 1380 cm^{-1} appeared while the band at 718 cm^{-1} characteristic for cyclohexene [10] disappeared. The presence of the band at 800 cm^{-1} characteristic for trisubstituted alkene and that at 1380 cm^{-1} for the CH_3 group is an indication for cyclohexene isomerization to 1-methyl-cyclopentene. This reaction has been already observed in the presence of alumina containing Ti and Na [14].

3.2. CYCLOHEXYLMETHANOL ADSORPTION

The new bands observed in the IR spectra of the adsorbed cyclohexylmethanol are presented in table 3. In this case the bands of the reaction products appeared at higher temperature due to the lower reactivity of this alcohol. Its dehydration in the presence of TiH-ZSM-5 (1) and H-ZSM-5 started at 373 K and the bands at 3030 cm^{-1} for the gas and at 1512 cm^{-1} for the adsorbed species appeared simultaneously. From the presence of the bands at 3030 and 800 cm^{-1} we concluded that the main dehydration product was 1-methyl-cyclohexane [10]. If methylene–cyclohexane were formed the bands should be at 3070, 856 and 889 cm^{-1}.

In agreement with previous results [12] we interpreted the band at 1512 cm^{-1} as shifted –C=C–vibration after interaction with the acid sites of the zeolite. TiH-ZSM-5 (1) differs from ZSM-5 zeolites by the lack of activity in cyclohexylmethanol dehydrogenation. At 473 K all the three examined molecular sieves caused the destructive oxidation of the cyclohexylmethanol to CO and CO_2 (bands at 2180, 2120 and 2336 cm^{-1}).

4. Discussion

The IR spectra of the adsorbed cyclic alcohols gave evidence for the presence of acid and basic (hydrogen accepting) sites in the Ti-containing molecular sieves. The acid sites caused the dehydration to olefins and the isomerization. The basic sites are responsible for the formation of carbonyl compounds. The reactivity of these sites depended on the catalyst structure and the Ti-content. The interaction of anatase with aliphatic alcohols has been described in the literature [15,16]. The formation of alkoxides, preceding the dehydration and dehydrogenation, has been suggested. The dehydration selectivity increased in the order:

Table 3
Temperatures at which new bands appeared in the IR spectra of cyclohexylmethanol interacting with the studied catalysts

Catalyst	1700 cm^{-1}	3040 cm^{-1}	2180, 2120, 2336 cm^{-1}	1512 cm^{-1}
TiH-ZSM-5 (1)	–	373	473	373
H-ZSM-5 (Si/Al = 50)	473	373	473	373
Cs-ZSM-5 (Si/Al = 50)	423	–	473	–

$$\mathrm{MeO} < \mathrm{EtO} < n\text{-}\mathrm{PrO} < i\text{-}\mathrm{PrO}\,.$$

The alkoxides were formed as a result of alcohol deprotonation on the surface oxygen anions near the coordinatively unsaturated Ti-cations. This means that the Ti-cations may be considered as mild Lewis acid sites [5] which influence the ability of neighboring oxygen anions to attach protons, i.e. the basic properties. According to our results and in agreement with ref. [6] the anatase does not possess any acid sites and only basic ones. In the IR spectra of TS-1 (fig. 4) we observed some OH-group bands (3480, 3725 cm^{-1}) that might explain its weak acid properties. The acid properties were improved by introduction of aluminum. TiH-ZSM-5 (1) and (2) possess similar acid and base properties. Their Na-forms have no acid sites. The higher concentration of Ti leads to a higher oxidation ability, revealed by the presence of the IR bands of CO and CO_2 (tables 1–3). The action of the acid and the base active sites might be limited by the alcohol reactivity depending on the bond energy and the intermolecular interactions [12]. The ability of cyclohexylmethanol to alpha- and beta-elimination of hydrogen was much lower than that of cyclohexanol. The water elimination from this molecule occurs at the same temperature in the presence of H-ZSM-5 and TiH-ZSM-5 (1). No dehydrogenation occurred on the Ti-pentasil, indicating that the basic properties of the last were much weaker. Cs-cations improved the basic properties and the dehydrogenation occurred at lower temperature.

5. Conclusions

The comparison of anatase with TS-1 and Ti-containing pentasils permitted to follow the changes in the catalytic properties with the composition. Anatase has basic properties and activates alcohol dehydrogenation. TS-1 has basic and weak acid functions activating the alcohol dehydrogenation and dehydration. Ti-containing pentasils have also basic and stronger acidic character and activate the isomerization of cyclohexene to methyl-cyclopentene.

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