ACID-BASE PROPERTIES OF ZEOLITES BY ACETIC ACID TEMPERATURE PROGRAMMED DESORPTION

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ABSTRACT

A new method based on temperature programmed desorption (TPD) of acetic acid is proposed to characterize acid-base properties of modified zeolites. The main desorption peak is associated with the generation of acid-base pairs in Mg-modified ZSM5 and alkaline cation exchanged X zeolites. The formation of acetate-like species is also suggested.

INTRODUCTION

Zeolites are well known for their acid properties, on which their catalytic activity for various petrochemical reactions is based. By contrast, their base properties have received little attention. The indicator technique for basicity determination was considered not suitable for zeolites by Yashima [1], due to their very low base site strength and concentration. On the other hand, examples of zeolite catalytic activity for base site-requiring reactions are known [2], suggesting the presence of base centres at relatively high concentration.

The properties of zeolites containing alkaline cations have recently been described in terms of conjugate acid-base pairs by Barthomeuf *et al.* [3]. Infrared studies of adsorbed pyrrole or benzene were used to evaluate the basic strength of different zeolites [3,4]. Thermogravimetric and IR spectroscopic studies of acetic acid adsorbed on faujasite-type zeolites for the characterization of the strength and catalytic behaviour of base centres [5, 6] have been reported.

In this paper, we propose a new method based on temperature programmed desorption (TPD) of acetic acid for the characterization of acid-base properties

of modified ZSM5 and X zeolites.

EXPERIMENTAL

Commercial NaX samples were cation exchanged with CsCl and CsOH solutions. Synthesized ZSM5 samples (Si/Al = 17) were obtained in H-form (HZSM5) through conventional procedure. HZSM5 samples were modified by ion exchanging or dry impregnating with $Mg(CH_3COO)_2$ aqueous solution. All samples were dried at 120 °C and calcined at 500 °C (zeolite X) and 540 °C (zeolite ZSM5). The chemical composition of modified zeolites was determined by atomic absorption analysis. The following materials were obtained:

MgZ1   prepared by impregnation of HZSM5, containing 4.2 MgO wt%
MgZ2   prepared by impregnation of HZSM5, containing 22.0 MgO wt%
MgZ   prepared by ion exchange of HZSM5, containing 2.3 MgO wt%
γ-Al_2O_3 prepared by thermal treatment of AlOOH at 550 °C
MgO   prepared by thermal decomposition of magnesium acetate at 550 °C
MgAl   prepared by impregnation of AlOOH with magnesium acetate, containing 22.0 MgO wt%
CsX1   prepared by ion exchange of zeolite X with CsCl, containing 35.3 Cs wt%
CsX2   prepared by ion exchange of zeolite X with CsOH, containing 35.7 Cs wt%
CsX3   prepared by impregnation of zeolite X with CsCl, containing 2.7 Cs wt%

The experimental apparatus for acetic acid TPD is illustrated schematically in Fig.1. Zeolite samples (0.5÷1.0 g) were loaded into a quartz tube (8 mm i.d.) connected upstream to the acetic acid feeding system and downstream to a thermal conductivity detector. The tubular reactor was heated by an electrical oven driven by a Linseis L 70 temperature programmer. The temperature of the sample was measured by a NiCr thermocouple moving in a sheath axially mounted in the quartz tube. Acetic acid was fed by saturating a He stream at 30 °C. Concentration of 2.6% acetic acid in He was performed. Acetic acid was adsorbed on zeolite samples at 150 °C up to saturation. After adsorption, He flow at 100 ml min^{-1} was fed to desorb physically adsorbed acetic acid. Finally, TPD was started at a heating rate of 10 °C min^{-1} and He flow of 100 ml min^{-1}.
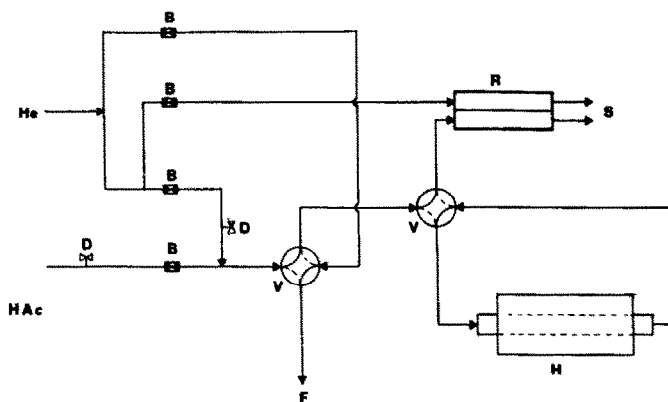
Fig. 1 Scheme of experimental apparatus for acetic acid TPD (B, flow control valve; D, ball valve; F, flowmeter; H, electric oven; R, thermal conductivity detector; S, vent; V, four-ways valve).

TABLE 1

Temperature of acetic acid desorption peaks.

Sample	$T_\alpha/$°C	$T_\beta/$°C	$T_\gamma/$°C
ZSM5	293		405-585
MgZ	293	323	543
MgZ1	a	320	543
		341°	
MgZ2	a	320	507
		352°	
MgO	-	352°	
γ-Al$_2$O$_3$	-	388°	418
MgAl	-	346°	447
		394°	
NaX	270	445	585
CsX1	282	435	
CsX2	285	440	
CsX3	270	440	573

a, not measurable; β peaks refer to acid-base pairs in zeolite; ° peaks associated with acid-base pairs in metal oxides.
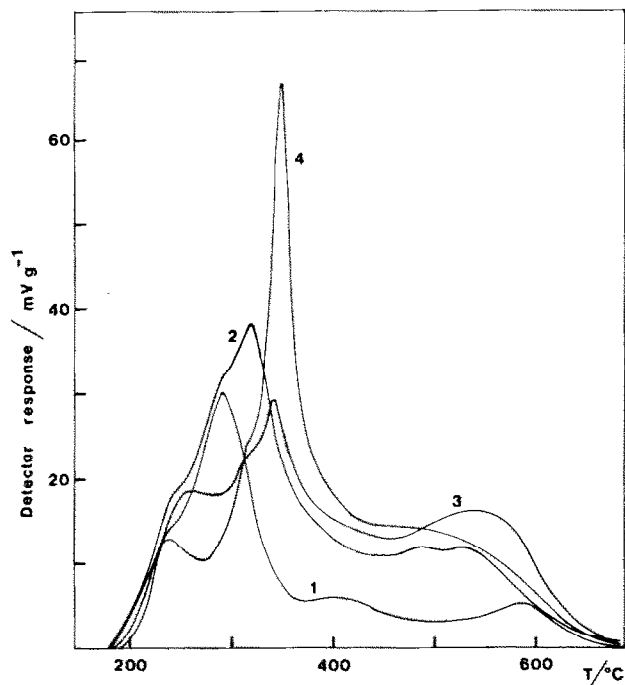
Fig. 2. Acetic acid TPD of ZSM5:(1) HZSM5; (2) MgZ; (3) MgZ1; (4) MgZ2.

RESULTS AND DISCUSSION

The pattern of the acetic acid TPD spectra was similar for all samples with three main peaks in the temperature ranges 240-300, 315-460, 500-650, α, β and γ peaks, respectively (Figs. 2 and 3 and Table 1).

Zeolite HZSM5 displayed α peak at 293 °C. A shoulder at 245 °C was also observed. A similar signal at about 250 °C was detected for all the materials. It can thus be regarded as associated with weak adsorption and not specific for zeolite interaction.

The modification with magnesium introduced by ion exchange or impregnation resulted in reduction of the α peak intensity (Fig. 2) in function of the Mg content. In sample MgZ1 it was impossible to resolve the peak, and in MgZ2 it was no longer detectable.

A similar behaviour was observed with zeolite X (Fig. 3). The exchange of Cs for Na cations resulted in a temperature shift from 270 to 280 °C, without intensity decrease in the α peak. Attribution of this peak is not easy. It seems to be specific for zeolite, not influenced by ion exchange but changed by impre-
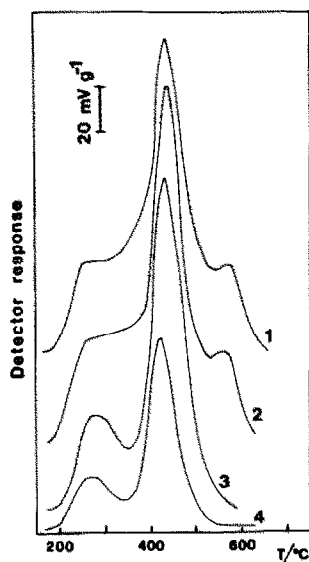
Fig. 3. Acetic acid TPD of zeolite X: (1) NaX; (2) CsX3; (3) CsX2;(4) CsX1.

gnation in the case of ZSM5 zeolite. Since the modification by impregnation reduced the internal volume of zeolite [7], the α peak could be due to acetic acid still physically adsorbed in the cavities. As effect of ion exchange the concentration of acetic acid for CsX1 and CsX2, if evaluated with reference to the zeolite unit cell, is reduced by about 25%, in accordance with the reduction of internal volume [7].

The high temperature γ peak indicated a very strong interaction of acetic acid with zeolite. It was detected for NaX and CsX3, but disappeared in CsX1 and CsX2. It appeared as a broad signal in the case of MgZSM5 in a temperature range lower than for zeolite X. The formation of acetate-like species very stable at high temperature has been reported [5] from IR studies of faujasite-type zeolites. We suggest that the γ peak should be attributed to these species, whose different stability also explains its absence for CsX1 and CsX2 zeolite.

A similar signal at T>500 °C was exhibited by MgO prepared by thermal decomposition of $Mg(CH_3COO)_2$ (Fig. 4) and supports this attribution. Moreover, on following the thermal decomposition of pure magnesium acetate under the same experimental conditions, a broad signal in the same temperature range was evidenced, giving further support to this interpretation [7]. The γ peak detected in the HZSM5 sample is probably due to the reaction of acetic acid with zeolite OH groups, giving adsorbed acetate ions [5].
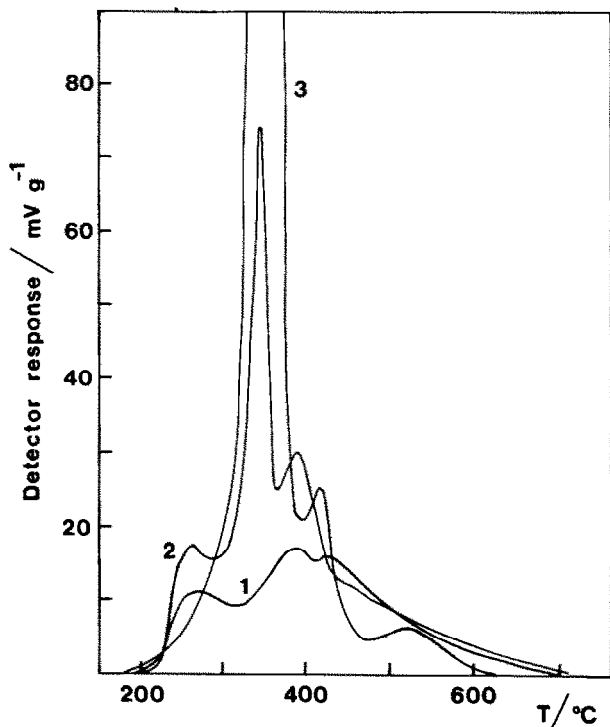
Fig. 4. Acetic acid TPD of reference materials:(1) γ-Al$_2$O$_3$; (2) MgAl; (3) MgO.

The medium temperature β peak appeared in the spectra of HZSM5 zeolite when it was modified by the introduction of magnesium. Samples impregnated or ion exchanged by magnesium acetate displayed this signal at about 320 °C. At higher magnesium concentration (MgZ1 and MgZ2 samples), a new signal at about 350 °C was superimposed. Its intensity was strongly dependent on the Mg content. The TPD curve of the MgO sample (Fig. 4) enabled us to attribute this signal to the presence of magnesium oxide formed on the external surface of ZSM5 zeolite, as was also shown by IR and X-ray investigation [7]. It may thus be suggested that the β peak is associated with the interaction with acid-base Mg^{2+}-O^{2-} pairs inside the zeolite. Various TPD spectra from reference materials were obtained to support this attribution. In the case of γ-Al$_2$O$_3$ prepared by thermal treatment of pseudobohemite, the peak at 388 °C (Fig. 4) can be associated with the interaction of acetic acid with aluminum-oxygen or hydroxyl-oxygen pairs. The same signal, shifted to 394 °C, was found for the mixed oxide MgO.Al$_2$O$_3$ (Fig.4), which displayed another peak with a comparable intensity at 346 °C. Following the principle of Sanderson [8] and

experimental IR and XPS results [9,10], introduction of magnesium in the structure of γ-Al$_2$O$_3$ results in a redistribution of the electrons whereby the basicity of oxygen is increased and the acid strength of OH groups and Al^{3+} and Mg^{2+} cations is decreased. Interaction with Mg^{2+}-O^{2-} and Al^{3+}-O^{2-} should be responsible for the two peaks detected for MgAl samples. Moreover, the peak cannot be associated with the interaction with Mg^{2+} alone, as no signal were detected in TPD of ammonia from MgO [7]. Furthermore, titration of acid-base pairs by acetic acid has been reported for HNaY zeolite [11].

In the case of zeolite X (Fig. 3), the β peak was displayed by samples at about 440 °C and can be associated with the same interaction. The higher temperature compared with the ZSM5 zeolite indicated a stronger interaction, due to the higher basicity of cation exchanged zeolite X, in accordance with the Sanderson electronegativity model [12].

These results are in agreement with those of Barthomeuf [3], who employed pyrrole adsorption to detect the basicity of zeolites. Nonetheless, this technique was unable to evidence the presence of basic sites in Cs exchanged ZSM zeolite, due to the low content of Al. In our experiments with Mg-modified ZSM5 zeolites, it seems that acetic acid TPD can detect acid-base pairs. Therefore, this tecnique should help to elucidate the acid-base properties of modified zeolites that influence their catalytic properties [7,12-14].

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