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EFFECT OF NON-SKELETAL Al SPECIES ON THE CONVERSION OF METHANOL PREADSORBED ON MODIFIED ZEOLITES

J. NOVÁKOVÁ and L. KUBELKOVÁ

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, 182 23 Prague 8, Czechoslovakia

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Temperature programmed description of small amounts of preadsorbed and converted methanol (TPD-C) was studied on acidic forms of modified Y zeolites. The modification consisted of generation of various types and amounts of non-skeletal Al species which yield Al Lewis acid sites, and, consequently, of changes of the number and strength of the Brönsted acid sites. All the non-skeletal Al species enhanced the methanol conversion to products whose composition was dependent on their properties as well as on the remaining skeletal hydroxyls.

1. Introduction

Conversion of methanol to hydrocarbons over zeolites is commonly assumed to be catalyzed by their skeletal hydroxyls [1] while the role of non-skeletal Al species has not yet been widely discussed. A positive role of Al species in methanol conversion to dimethylether has been reported in some papers [2,3]. However, under usual catalytic conditions, their presence most probably enhances the process of deactivation [4]. This paper is an attempt to demonstrate the influence of various Al species on the conversion of small amounts of preadsorbed methanol, i.e. on the most intimate steps in the interaction including the primary C-C bond formation. Acidic forms of Y zeolites were used without and with modifications carried out by (i) dehydroxylation, (ii) cationic Al exchange, (iii) hydrothermal treatment and (iv) dealumination with $SiCl_4$. In some cases, non-skeletal Al species were extracted by H_2Na_2EDTA to investigate the effect of the dealumination of the lattice alone. The acidity of the zeolites under study was characterized by temperature programmed desorption (TPD) of ammonia and by adsorption of pyridine.

2. Experimental

Zeolites. The zeolites used, their composition and characterization of acidity are given in table 1. Samples $H_{70}Na_{30}$-Y (HNaY, No 1) and $H_{95}Na_5$-Y (HY, No 4)

Table 1
Characteristics of zeolites used

No	Zeolite	$T_{act.}$ °C	Sorption capacity [a] mmol g^{-1}	Si/Al total	Si/Al skeleton	PyAl [a] mmol g^{-1}	TPD of ammonia	
							acid sites [a] mmol g^{-1}	T_{max} °C
1	HNaY	400	10.9	2.5	2.5	0.04	3.35	250
1a	HNaY	510 [b]	10.9	2.5	–	0.53	2.45	200
2	AlHNaY	400	10.4	2.24	2.5	0.3	3.1	190
3	HNaY-US	400	9.1	2.5	4.48	0.11	1.4	80
4	HY	350	10.4	2.9	2.9	0.03	4.3	250
4a	HY	620	10.4	2.9	–	0.74	1.6	130
5	HY-US	400	9.1	2.9	6.14	0.15	2.2	200
6	dealY-ex	400	9.3	5.6	5.67	0.04	3.1	260
7	dealY	400	9.2	3.4	5.67	0.35	1.9	250

[a] per g of dried sample.
[b] 3 hrs only.

were supplied in the ammonium form by the Research Institute for Oil and Hydrocarbon Gases, Czechoslovakia. $H_{34}Al_{12}Na_{30}$-Y was prepared by ion exchange from sample No 1 with 0.1M $Al(NO_3)_3$ at pH 4 (AlNaHY, No 2). Hydrothermally modified zeolites denoted US (Nos 3 and 5) were prepared from samples 1 and 4, respectively, under selfsteaming conditions at 770 °C [5,6]. Dealuminated zeolite (No 7) was the product of $SiCl_4$ treatment of dehydrated NaY at 300 °C, followed by washing with water and NH_4^+ exchange ([7], procedure B). Extraction of this zeolite with H_2Na_2EDTA described in detail in [6], yielded sample No 6.

Dehydration and deammoniation of all the zeolites used were carried out at 350–400 °C in a vacuum of 10^{-4}Pa for 18 hrs and dehydroxylation of some samples proceeded at temperatures higher than 500 °C (see table 1). The modified zeolites exhibited good crystallinity which was checked using RTG diffraction patterns, the infrared spectra of skeletal vibrations and the sorption capacities shown in table 1. IR spectra of skeletal vibrations were also used in the combination with wet chemical analysis to calculate the total Si/Al ratio in the zeolite skeleton ([6], table 1).

Acidity measurements. In the TPD of ammonia, 6 mmol g^{-1} of ammonia were adsorbed on the zeolite (0.01 g) at 25 °C and desorbed with a heating rate 6 °C min^{-1} into a MCH 1302 mass spectrometer (USSR). The fragment peak $m/z = 16$ was used to characterize the desorbed ammonia. As the decomposition of the ammonium form of sample 1 gave the same m/z-temperature plot as the desorption of ammonia from this zeolite (see fig. 1, dotted and full lines of the sample No 1), the area under this curve was used to quantify the number of acid sites. In the pyridine interaction with zeolites, an excess of pyridine was adsorbed

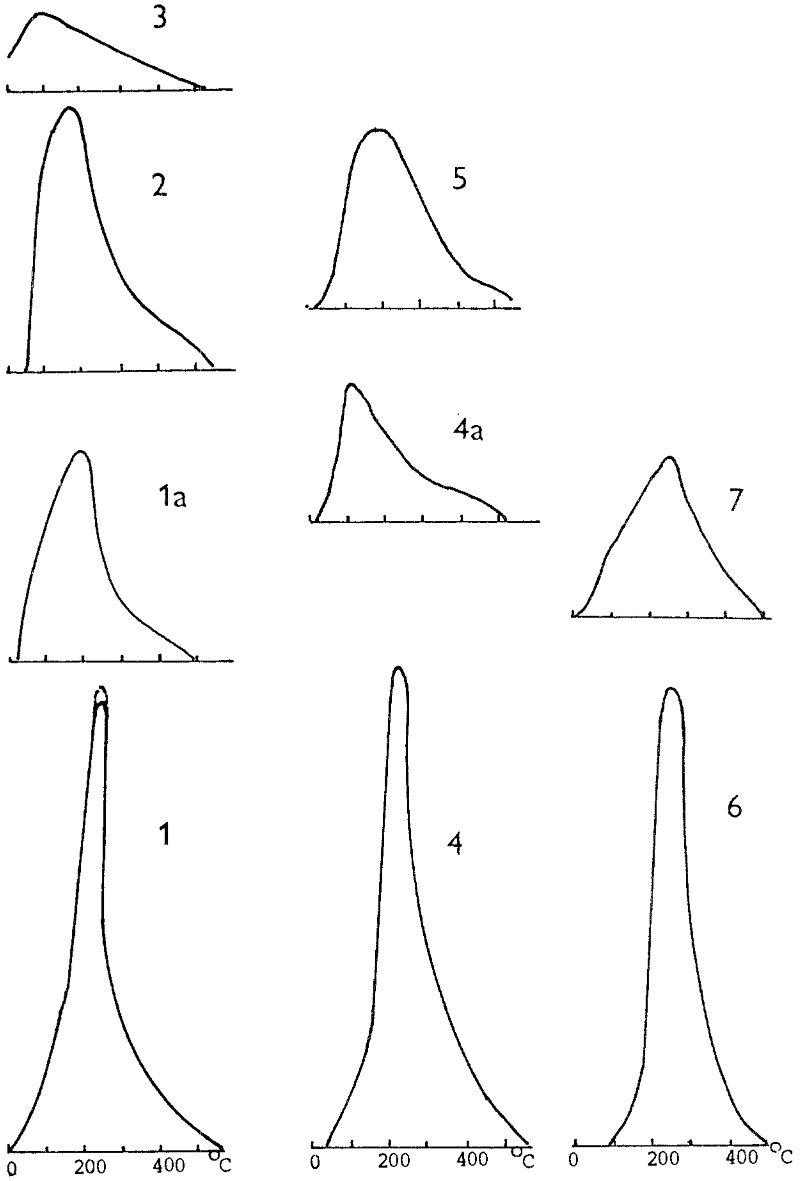

Fig. 1. TPD of ammonia. Numbering of the zeolites as in table 1; ordinate: height of the fragment peak $m/z = 16$, in arbitrary units.

at 150 ° C on a zeolite plate 7 mg cm^{-2} in thickness and desorbed at 250 ° C. The number of strong pyridine-Al complexes (PyAl) was calculated from the height of the infrared band at 1454 cm^{-1} according to ref. [8]. Infrared spectra were recorded by means of a Nicolet MX-1E Fourier transform infrared spectrometer.

Reactivity measurements (TPD-C). 0.03 mmol g^{-1} of methanol were adsorbed on the zeolite (0.1 g) at 25 ° C and desorbed with a heating rate of 5 ° C min^{-1} into a

Finnigan 400 quadrupole mass spectrometer. Mass spectra were normalized using typical fragment peaks, their abundance in the relevant spectrum and ionization cross sections.

3. Results and discussion

Three samples, HNaY, HY and dealuminated Y after extraction of non-skeletal Al (Nos. 1, 4 and 6) contain almost only Brönsted acid sites, i.e. bridging hydroxyls on the skeleton, $\mathrm{Si-\overset{\overset{\displaystyle H}{|}}{O}-Al}$. This follows from table 1: the amount of PyAl is negligible, and the numbers of acid sites calculated from the TPD of ammonia correspond closely to the theoretical values, 3.6, 4.2 and 2.7, respectively. The relevant TPD curves of ammonia (fig. 1, curves, 1, 4, 6) exhibit symmetrical high peaks with maxima at 250–260 °C. However, the conversion of adsorbed methanol is relatively very low: at about 150 °C a large amount of unreacted methanol is released, followed by a rather small amount of dimethylether (DME), olefins and aromatics (fig. 2, samples 1, 4, 6; aromatics are always accompanied by hydrogen release, not shown in fig. 2). The low activity most probably results from the small number of methoxyls formed, $\mathrm{Si-\overset{\overset{\displaystyle CH_3}{|}}{O}-Al}$, [9,10] (the decisive role of methoxyls in the formation of DME and as precursors in the generation of primary C-C bonds was also proposed in [11–14]). The increased Si/Al ratio of the zeolite skeleton of sample No 6 does not influence the composition of the products, and only olefins appear at a lower temperature.

The modifications used preserve the Si/Al_{total} ratio (table 1), of course with the exception of Al added by ion exchange (No 2) or substituted by Si and removed (Nos 6 and 7). All of them are accompanied with a change in the Al distribution resulting in an increase of the $Si/Al_{skeleton}$ ratio and appearance of non-skeletal Al. The $Si/Al_{skeleton}$ ratio could not be measured with dehydroxylated zeolites; however, at least a part of the skeletal Al atoms loses tetrahedral coordination as follows from the formation of AlPy complexes with strong electron-accepting (Lewis) acid sites. As can be seen in table 1, the total number of acid sites decreases as does their acidity strength. The desorption rate maxima are shifted to lower temperatures, and the shape of the ammonia TPD curve is disturbed (fig. 1, curves 1a, 2, 3, 4a, 5 and 7), most probably because of the presence of heterogeneous Al electron accepting sites, which do not exhibit a well-resolved peak. The conversion of adsorbed methanol, both to DME and hydrocarbons, substantially increases, apparently as a result of the formation of methoxy groups bound to Al species, CH_3O-Al, and their reactivity with physisorbed methanol, CH_3OH..Al to DME at lower temperature [9,10]. This occurs

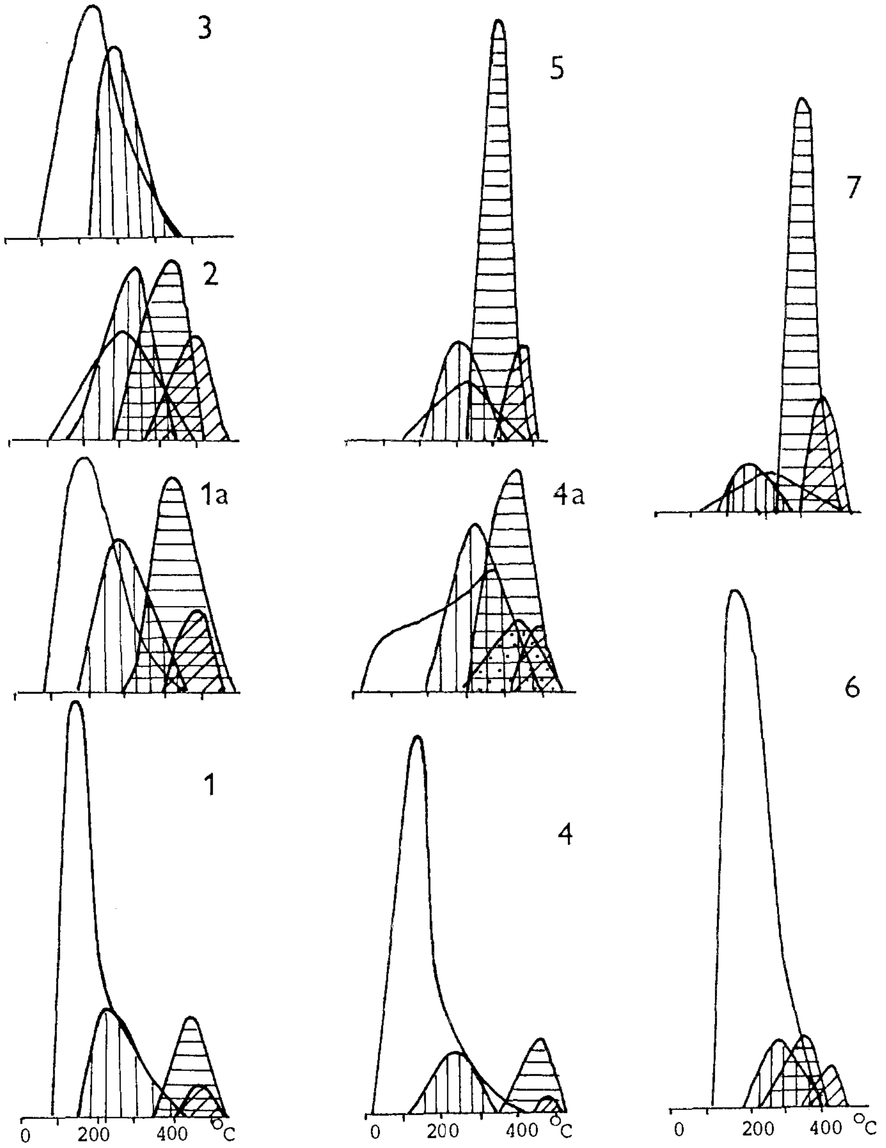

Fig. 2. TPD-C of preadsorbed methanol. Numbering of the zeolites as in table 1, ordinate: normalized products, in arbitrary units, □ methanol, ▥ DME, ▤ olefins C_{2-4}, ▨ aromatics C_{7-11}, ⊡ methane.

exclusively in sample No 3 which contains only a small number of weak acid sites. On samples possessing higher numbers of stronger Lewis acid sites together with some remaining stronger hydroxyls (Nos 1a, 2, 5, 7), the methoxyls react at higher temperatures to primary olefins either with reformed methanol [10] or with remnants of the physisorbed methanol (the maxima of its desorption lie at temperatures higher than for samples 1, 4 and 6 and are flatter), or, in an appropriate case, via the inter-reactions of methoxyls. Higher hydrocarbons and aromatics are then formed via the commonly assumed mechanisms (carbocations, hydrogen transfer, condensation, cyclization etc.). Methane and traces of formaldehyde also appear in the products of methanol conversion on strongly dehydroxylated zeolite HY (No 4a) and also on more dehydroxylated HNaY (not shown here). This was previously found for some HZSM-5 zeolites [9,10] and the formation of these products was assumed to proceed via the disproportionation of methoxyls, one of which at least is bound to Al.

4. Conclusions

All non-skeletal Al species in acid forms of Y zeolites enhance the conversion of adsorbed methanol. The composition of the products, however, depends on the number and the acidity strength of both the Lewis acid sites and the remaining skeletal hydroxyls. The adsorbed methanol can thus be converted not only to DME, but also to olefins and aromatics and methane with formaldehyde.

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