Methanol adsorption and dehydration on alkali metal exchanged NaY zeolites

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FT-IR spectroscopy has been applied in a study of methanol adsorption on M^INaY zeolites (M = Li, K, Rb, Cs). Coordinatively and/or hydrogen bonded methanol was registered in the temperature range 300–473 K. Dehydration of methanol to dimethyl ether occurred at 573 and 623 K. It was found that the activity of the catalyst for methanol dehydration strongly depends on the kind of alkali metal cation, and well correlates the IR data relative to methanol adsorption.

Keywords: M^INaY zeolites; methanol adsorption and dehydration; FT-IR spectroscopy

1. Introduction

Methanol is a sensitive probe molecule to determine the surface properties of metal oxides by infrared spectroscopy. In particular, the wavenumbers of $\nu(CH_3)$ vibrations depend on its adsorption mode: coordinatively methanol adsorbed species are characterized by high $\nu(CH_3)$ wavenumbers [1] whereas dissociated methanol forming methoxy groups leads to low $\nu(CH_3)$ frequencies [2]. Methanol is also a reactant giving rise to dimethyl ether on acidic surfaces [3]. The aim of the present paper is to relate infrared data obtained for methanol adsorption on different M^INaY zeolites to their reactivity in dimethyl ether formation.

2. Experimental

Zeolite NaY (Katalistiks) with initial composition $Na_{54}(AlO_2)_{54}(SiO_2)_{138}$ and surface area 899 $m^2\ g^{-1}$ was used as parent material. Before the modification processes, the samples were treated twice with 1 M solution of NaCl to remove cations other than Na^+ and to bring the Al/Na ratio to equilibrium. Modified forms were prepared by an ion exchange with 0.2 M solutions of respective alkali metal nitrates. The catalysts so obtained are listed in table 1. The zeolite structure was preserved after modification.

The chemical composition of exchanged zeolites was determined by a chemical analysis: SiO_2 gravimetrically, aluminium by EDTA titration and Li, K, Rb and Cs by atomic absorption spectroscopy (Unicam SP-90 instrument).

The samples were investigated by means of FT-IR spectroscopy. Self-supporting wafers (10 mg) were prepared and activated in vacuum by heating them (100 K h^{-1}) up to 523 K, leaving them at this temperature for 2 h, then heating to 673 K (100 K h^{-1}) and keeping them at 673 K for 9 h, and if necessary, 30 min in an oxygen atmosphere to remove carbonates. IR spectra were recorded by a Nicolet MX60 Fourier transform spectrometer (resolution 4 cm^{-1}).

Small quantities (up to 598 mmol/g) of methanol were introduced at room temperature (RT), then the temperature was increased (10 K min^{-1}) to 373, 473, 573 and 623 K without evacuation.

3. Results

Adsorption of methanol on M^INaY (M = Li, K, Rb, Cs) at room temperature did not show dissociation of the CH_3OH molecules since no $\nu(OH)$ band was observed in the 3800–3600 cm^{-1} frequency range. The changes in IR spectra resulting from the increasing amount of methanol adsorbed at room temperature were similar for all zeolites used. An example is shown in fig. 1 for LiNaY. With the increasing amount of methanol introduced the bands due to the CH_3 vibrations at ~ 2960 and 2852 cm^{-1} as well as those relative to

Table 1
Composition of the samples used

Catalyst	Na/Al	M/Al
LiNaY	0.59	0.41
KNaY	0.37	0.55
RbNaY	0.41	0.59
CsNaY	0.31	0.68

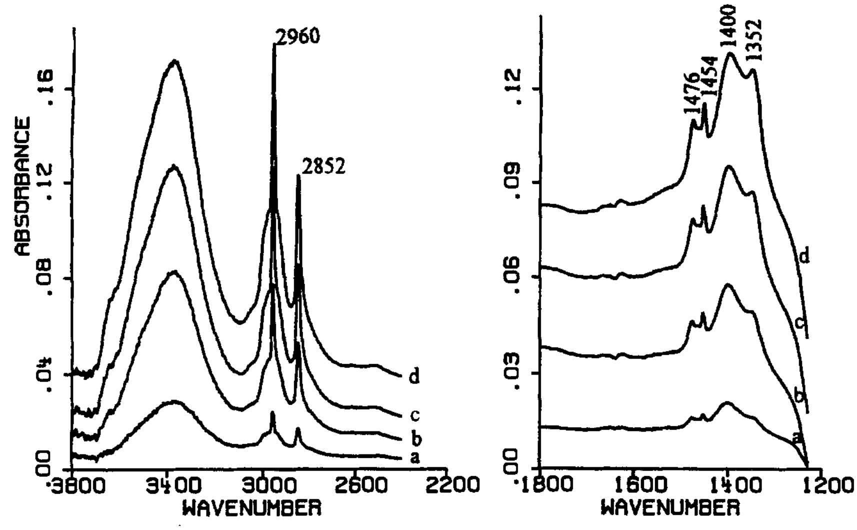


Fig. 1. FT-IR spectra of species given by methanol introduction on LiNaY at room temperature: (a) 85, (b) 256, (c) 427 and (d) 598 μmol g^{-1}.

hydroxyl groups (a broad ν(OH) band at ~ 3400 cm^{-1}) became more visible. It is worth to note that the wavenumber of the $\nu(CH_3)$ bands depends on the kind of alkali metal cation in the zeolite (table 2, fig. 2). It is always higher than those observed for CH_3OH in CCl_4 solution [1], showing the formation of methanol coordinated species. The shift of the presented bands indicates the interaction between the formed species and alkali metal cations: the strength of CH_3OH coordination decreases from Li to Cs forms of zeolites, due to the decrease of the electronegativity of the cation.

In the 1800–1200 cm^{-1} region some changes, depending on the type of cations, were registered after methanol adsorption at room temperature. They are shown in fig. 2. The bands between 1400 and 1450 cm^{-1} can be due to methanol $\delta(CH_3)$ vibrations. In agreement to that, the position of the band at ~ 1450 cm^{-1} slightly depends on the nature of the cation which confirms that some bands are sensitive to the cation interaction as observed for $\nu(CH_3)$ wavenumbers. The band at about 1650 cm^{-1}, the most evident on NaY, is due to water traces, possibly a contaminant of methanol. The broad band at about 1400 cm^{-1} is assigned to the δ(OH) vibration, confirming the formation of coordinated species. Evacuation at increasing temperature indeed showed a concomitant decrease of the intensity of both broad bands at about 3400 and 1400 cm^{-1}.

The transformation of chemisorbed methanol upon

Table 2
$\nu(CH_3)$ wavenumbers of CH_3OH species adsorbed on the samples used

Zeolite	IR band wavenumber (cm^{-1})	
LiNaY	2960	2852
NaY	2959	2849
KNaY	2954	2841
RbNaY	2952	2837
CsNaY	2940	2829

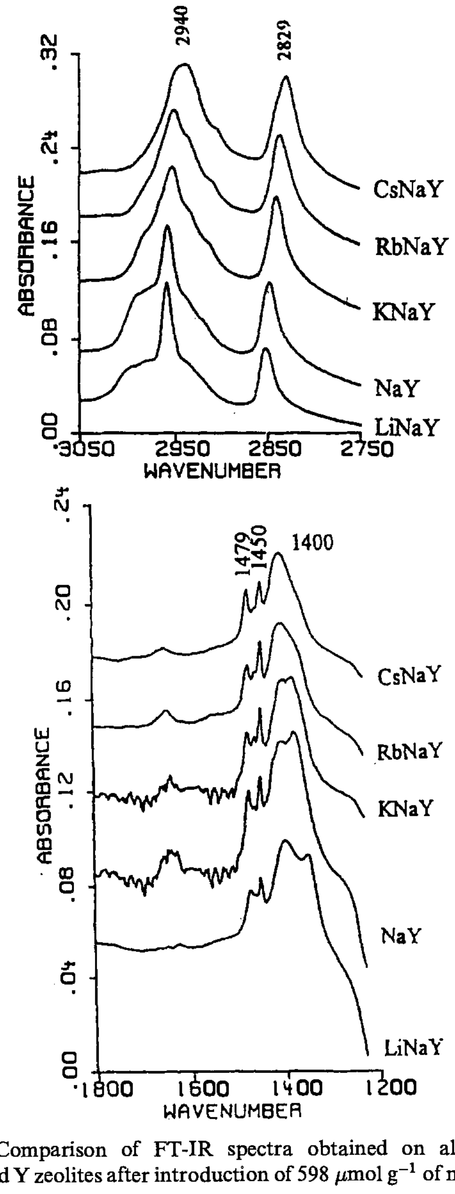


Fig. 2. Comparison of FT-IR spectra obtained on alkali metal exchanged Y zeolites after introduction of 598 μmol g^{-1} of methanol at room temperature.

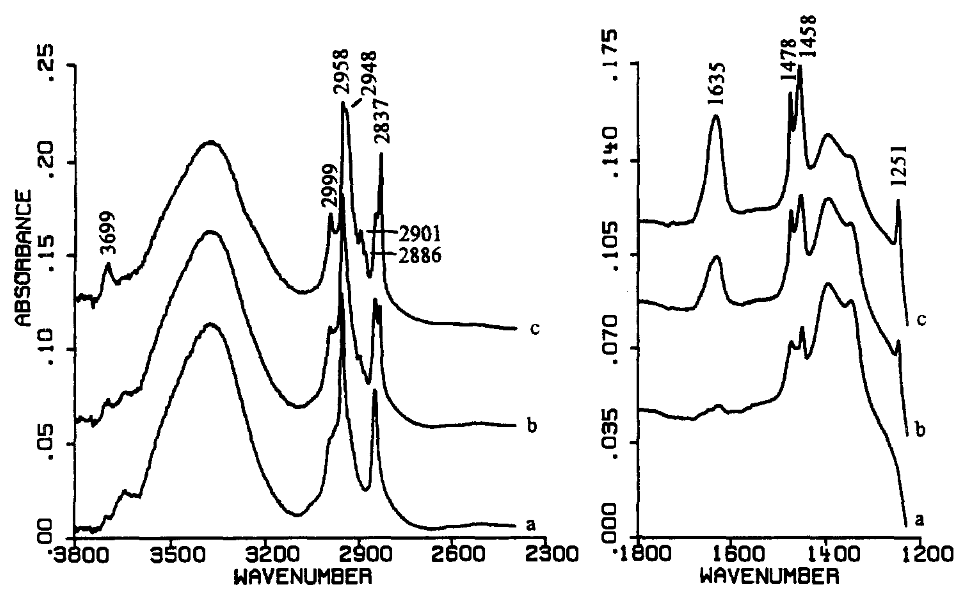


Fig. 3. FT-IR spectra of species given by methanol introduction on LiNaY (598 μmol g^{-1}) and after heating at (a) 473, (b) 573 and (c) 623 K.

heating up to 623 K can be observed in fig. 3 which shows the IR spectra registered for LiNaY. The spectra obtained after heating at 373 and 473 K are the same as at room temperature. From 573 K one can observe changes in IR spectra which became more visible after heating at 623 K. On LiNaY (fig. 3), in the $\nu(CH_3)$ region, a sharp band at 2837 cm^{-1}, a shoulder at ~ 2948 cm^{-1} and a weak band at 2999 cm^{-1} are formed. Comparison with spectra obtained from $(CH_3)_2O$ adsorbed on NaY (fig. 4) allows one to assign them to dimethyl ether formation. This is confirmed by the intensity increase of bands at 1478 and 1458 cm^{-1} and by the appearance of a new band at 1251 cm^{-1}. The other weak bands at 2886 and 2901 cm^{-1} most probably also belong to dimethyl ether. The 1635 cm^{-1} band, assigned to water, confirms methanol dehydration. The intensity of this band increases with temperature, as that at 3699 cm^{-1}. The latter can be due to water or to non-acidic OH groups resulting from water adsorption.

All these features have been observed for all the zeolites used. An important point is the formation of dimethyl ether well characterized by a band near 1250 cm^{-1}. Fig. 5 reports the spectra observed in this range with those relative to the δ(HOH) (1700–1600 cm^{-1}) and ν(OH) bands. It is clearly seen that the 1250 cm^{-1} band appears simultaneously with the δ(HOH) and ν(OH) bands, except in the case of CsNaY where almost no ν(OH) band is detected. By increasing the temperature, the intensity of the broad band at ~ 3370 cm^{-1} originating from methanol species decreases.

One should stress that all described experiments were carried out without evacuation of the excess of methanol, so, during heating the interaction between chemisorbed species and methanol in the gas phase could occur.

4. Discussion

IR spectroscopy analysis of species formed from methanol adsorption on M^INaY zeolites shows : (i) a dependence of the $\nu(CH_3)$ vibrations on the nature of

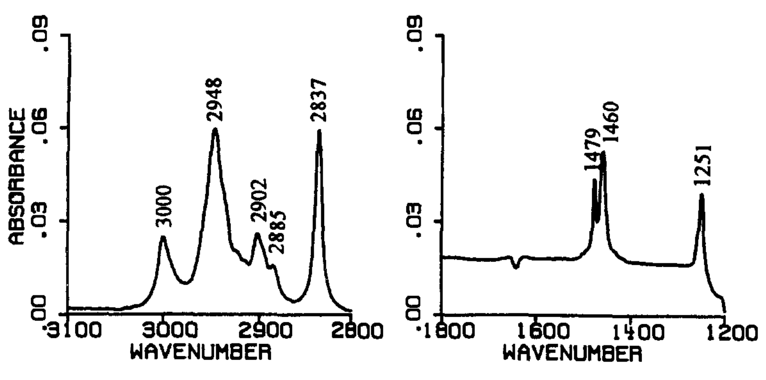


Fig. 4. FT-IR spectrum of dimethyl ether adsorbed on NaY at room temperature.

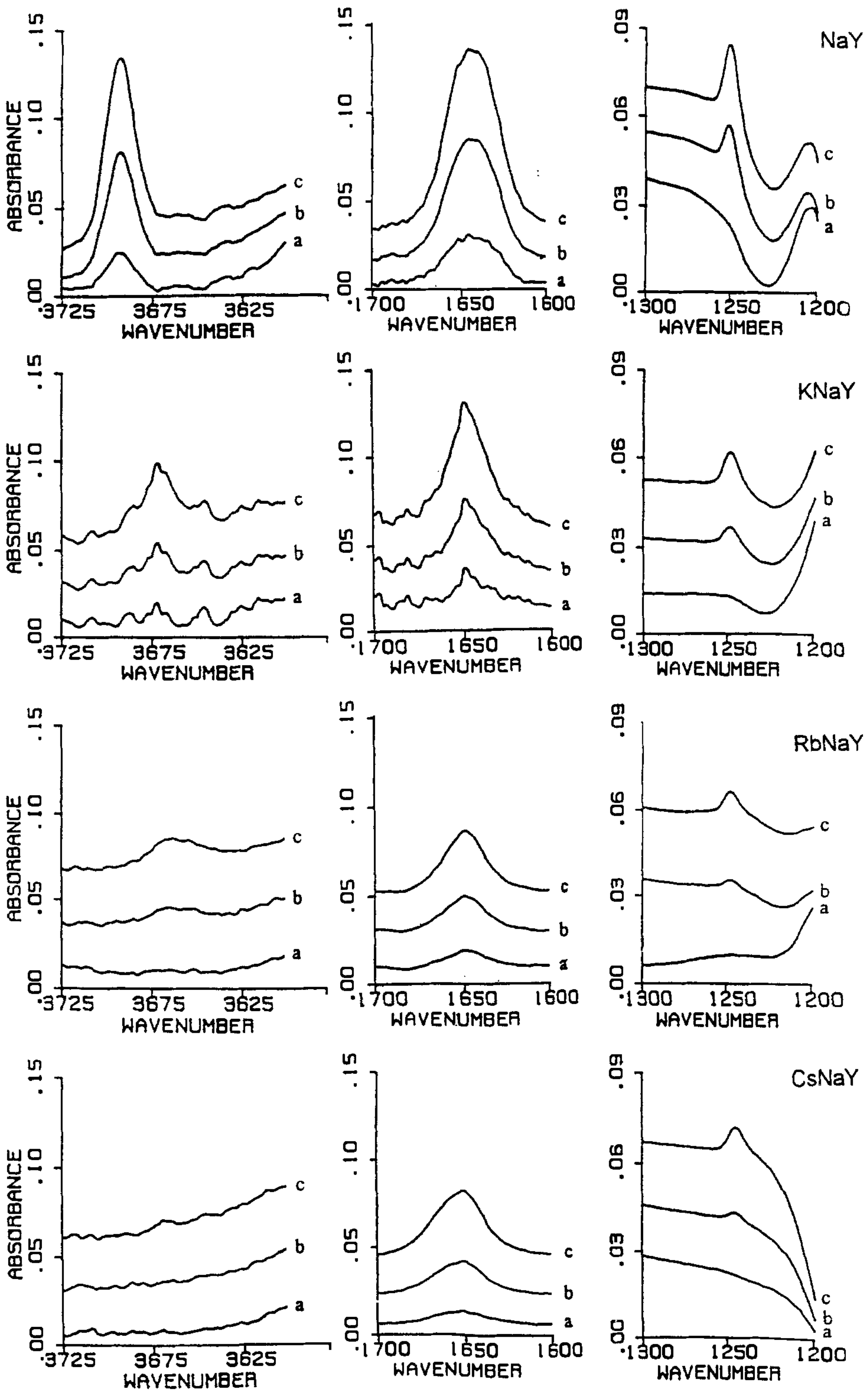
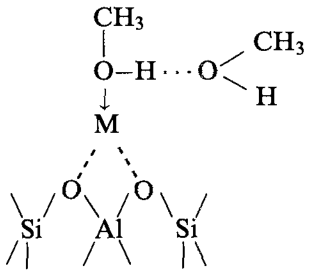


Fig. 5. FT-IR spectra of species given by methanol introduction (598 μmol g^{-1}) on alkali metal exchanged zeolites and after heating at (a) 473, (b) 573 and (c) 623 K.

the alkali metal cation, which means that the cation is directly involved in the interaction, (ii) the presence of hydrogen bonded species characterized by a low ν(OH) frequency and a high δ(OH) wavenumber. From these results, and taking into account results in refs. [5,6], two possibilities of adsorption can be proposed:



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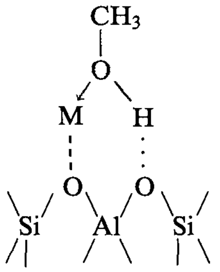

II

Species I have already been observed on Al_2O_3 [1]; the formation of (1 : 2) complexes is due to an increase of the acidity of the first molecule coordinatively bonded which favors an interaction with the second one [4]. Species of type II has been proposed on M^IX zeolites by Philippou and Anderson [5] from NMR results but at higher temperature. Type II is preferred because formation of type I should give rise to a more complex spectrum in the $\nu(CH_3)$ frequency range as the $\nu(CH_3)$ bands of the first coordinated molecule should be different from that of the second molecule, hydrogen bonded.

Heating under excess of methanol above 573 K leads to formation of dimethyl ether as shown in figs. 3 and 5. This formation is confirmed by that of water. Fig. 5 shows that increase of the cation size in zeolite gives rise to a decrease of the amount of dimethyl ether and water produced. Current experiments on pyridine adsorption on the same samples show that the strength of the cation Lewis sites decreases from LiNaY to CsNaY, in agreement with [7]. On the other hand, the Lewis basicity increases in the opposite way [8]. The present results therefore confirm that dimethyl ether formation from methanol is favored by catalysts presenting a high Lewis acidity and a low basicity. The activity order found from the amount of chemisorbed dimethyl ether formed: LiNaY > NaY > RbNaY ≈ CsNaY is quite in agreement with the $\nu(CH_3)$ wavenumber decrease from LiNaY to CsNaY (table 2) and shows that the coordination strength of methanol plays an important role in its transformation into dimethyl ether.

The fact that in the case of M^INaY zeolites heated with methanol, the transformation of methanol occurs at lower temperature to compare with M^INaX reported in ref. [5] is in agreement with the present results since the M^INaY zeolites present stronger cationic acid sites and lower basic sites than the corresponding M^INaX materials [8].

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