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Dedicated to Professor Valer Fărcăşan
at his 85th anniversary

INTERACTIONS OF METHANOL WITH $AlPO_4$-5 AND SAPO-5 SINGLE CRYSTALS

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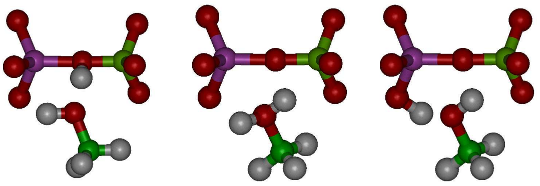
ABSTRACT. The interactions of methanol as polar probe molecule with the framework of $AlPO_4$-5 and SAPO-5 molecular sieves in the form of single large crystals were investigated with FT-IR micro-spectroscopy. Methanol exhibited weak interactions with $AlPO_4$-5. The polar molecules of methanol on SAPO-5 interacted primarily with the bridging OH groups. Polar molecules of methanol revealed a bimodal distribution of acid strength of the bridging OH groups. Two adsorbate species have been found to occur, both bound via hydrogen bonds of different strength dependent on the adsorption site. The interactions between the probe molecules and the framework are stronger in the confined environment of the narrow channels than in the wide channels. However, all these interactions are weak and do not lead to irreversible structure changes of $AlPO_4$-5 and SAPO-5 materials.

Keywords*:* $AlPO_4$-5 and SAPO-5; Single crystals; Adsorption of methanol, FT-IR spectroscopy

INTRODUCTION

Extensive IR spectroscopy studies of methanol [1,2] allowed the assignment of the bands at 3682 and 1080 cm^{-1} to the stretching and bending vibrations of OH groups in free methanol molecules, respectively. Associated methanol gave rise to new bands at around 3300 and 1340 cm^{-1}. They were assigned to the same hydroxyl group vibrations which underwent a red and blue shift, respectively, due to mutual interactions *via* hydrogen bonding. An increasing strength of the hydrogen bonding, *i.e.*, liquid and solid state of methanol, led to a further red shift of the OH stretching vibration to 3200 cm^{-1} and a blue shift of the OH bending vibration to around 1500 cm^{-1}.

Interpretation of the IR spectra of methanol adsorbed on acidic molecular sieves is especially complex and related to the question whether methanol is protonated by strong Brønsted acid sites or not. While Ison and Gorte [3] proposed that methanol occurs as strongly hydrogen bound species, Mirth *et al.* [4] and Jentys *et al.* [5] assigned certain patterns of bands to protonated methanol. The spectra of methanol adsorbed on zeolites were also assigned to the so called A-B-C patterns [6], caused by a Fermi resonance between the out-of-plane deformation vibrations of the bridging OH groups and the perturbed hydrogen bound OH groups. *Ab initio* studies by Haase and Sauer [7] supported the latter interpretation: strongly hydrogen bound methanol is the most favourable adsorption complex. As the energy difference between this neutral complex and an ion pair complex with protonated methanol is small, the authors proposed that the latter is a transition structure between the transfer of a proton from one oxygen atom to a neighbouring one *via* an adsorbed methanol molecule (Fig. 1). These calculations relate to a rather perfect environment and only one adsorbed methanol molecule per acid site. Calculations fail to explain fully the IR absorption band found normally between 3500 and 3630 cm^{-1}. Mirth *et al.* [4], assigned it to protonated methanol molecules which interact *via* methyl groups with $(SiOAl)^-$ groups of the framework. However, the calculations by Blaszkowski and van Santen [8] revealed the ratio between the number of methanol molecules interacting with the SiOHAl group *via* the hydroxyl group to those interacting *via* the methyl group to be equal to $4.5 \cdot 10^4$. Thus, in the light of the hydrogen-bonding model, the most convincing explanation seems to be that the OH group of alcohol is only weakly perturbed and shows such a small downward shift.



protonated methanol

Fig.1. Possible surface species of methanol interacting with the bridging hydroxyl group.

We aimed at a better understanding of acidic sites in $AlPO_4$-5 and SAPO-5 *via* determination of interactions between the metal substituted materials and methanol by means of highly sensitive IR studies. The probe compound has been chosen as relatively small dimension and high polarity able of penetration into the whole adsorption space of the molecular sieves. Moreover, methanol is an interesting compound used in numerous industrial processes such as *methanol-to-gasoline* (MTG) [9] or alkylation of aromatics [10]. The IR measurements were performed using *in situ* IR micro-spectroscopy on single large crystals of $AlPO_4$-5 and SAPO-5 that allowed us to avoid any intercrystalline effects.

EXPERIMENTAL

Synthesis of the $AlPO_4$-5 and SAPO-5 single crystals, the applied procedures, as well as the IR measurements methodology have been described in details elsewhere [11-15]. Absolute methanol (>99.8%, Merck) was used as probe molecule. The experiments were carried out in a vacuum cell, equipped with IR transparent windows, which was attached to the stage of a BRUKER IR microscope coupled to a BRUKER IFS 88 spectrometer. The calcined crystals were placed in the IR cell and heated at 10 K/min to 770 K under vacuum of 10^{-6} mbar for 30 min. After cooling down at 10 K/min to 310 K under vacuum, spectra of the selected crystals were recorded. The sorbates were introduced into the IR cell via a differentially pumped gas inlet system. The partial pressures (10^{-3} to 1 mbar) were hold constant until sorption/desorption equilibrium was achieved. The sorption was followed in situ by time resolved FT-IR micro-spectroscopy (1000 scans/spectrum, 4 cm^{-1} resolution). Subsequently, the cell was evacuated (10^{-6} mbar, 310 K) and temperature was increased to 775 K at 10 K/min.

RESULTS AND DISCUSSION

AlPO$_4$ –5. In contact with 10^{-1} mbar methanol, AlPO$_4$-5 showed the ν_{OH} bands at 3675 (negative), 3597 and 3178 cm^{-1}, and the band of the in-plane bending vibrations of the OH groups [4] at 1489 cm^{-1}. The ν_{CH} bands of methanol [4] were found at 2995(sh), 2960, 2925(sh) and at 2850 cm^{-1} (Fig. 2). Increase in pressure to 1 mbar led to a blue shift of the band at 3597 cm^{-1} to 3630 cm^{-1} and a shoulder at 3610 cm^{-1}. The broad absorption band at 3178 cm^{-1} shifted to 3228 cm^{-1} and had a shoulder at 3375 cm^{-1}. The CH stretching vibration bands grew in intensity. The last pressure step did not cause negative bands in the region of the OH stretching vibrations, which means that all accessible terminal P-OH groups were covered at 10^{-1} mbar.

The 3597 cm^{-1} band of methanol adsorbed on AlPO$_4$ –5 is assigned to a weakly perturbed stretching vibration of methanol OH hydrogen bound to the terminal P-OH groups (negative band at 3675 cm^{-1}). The corresponding deformation OH vibration of methanol was found at 1489 cm^{-1}. The ν_{OH} band at 3178 cm^{-1} is attributed to the perturbed terminal P-OH groups. The positions of these bands indicate a weak interaction of methanol with the P-OH groups. The presence of the relatively free vibrating methanol OH groups shows that the interaction of methanol with the framework is weaker than that of water [15]. The high frequency bands at 3630 and 3610 cm^{-1} stem from the free vibrating methanol OH groups. The broad bands at 3375 and 3228 cm^{-1} are assigned to methanol hydroxyl groups of the mutually interacting methanol molecules. The fact that the absorption bands occur in pairs can be explained by the different adsorption of methanol in the wide and narrow channels, in the latter with a higher strength of interaction due to a confined environment [12].

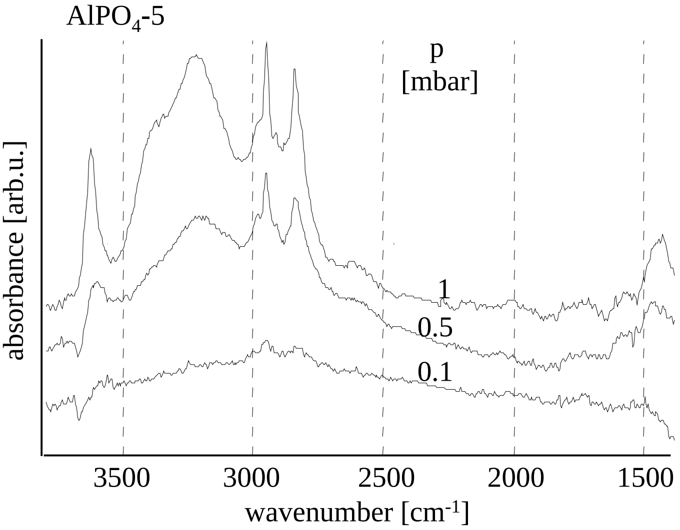


Fig. 2. Difference spectra between individual steps of the uptake of methanol in the pores of AlPO$_4$-5 single crystals.

SAPO-5. The spectrum of SAPO-5 in contact with methanol at a low pressure (10^{-1} mbar) showed negative bands of the stretching OH vibrations at 3632 and 3496 cm^{-1}, which were masked by a new positive v_{OH} band at 3568 cm^{-1}. The broad bands at ~3100, 2807 and 2473 cm^{-1} were assigned to the stretching vibrations of hydroxyl groups as well. The bands of the bending OH vibrations were found at 1735 and 1525 cm^{-1} (Fig. 3). Increase in pressure to 0.25 and 0.5 mbar led to an increase in intensities of all the bands and to a shift of the band at 3568 cm^{-1} to 3587 cm^{-1}. After the pressure raise to 1 mbar, new negative bands of stretching OH vibrations were found at 3733 and 3675 cm^{-1}, assigned to the terminal Si-OH and P-OH groups, respectively. The broad band from 3100 cm^{-1} appeared shifted to 3205 cm^{-1}. The negative absorption bands of the strong Brønsted acid sites at 3632 and 3496 cm^{-1} increased the intensity in parallel with those at 3598 (shifted from 3587 cm^{-1}), 2790, 1750, 1690 and 1525 cm^{-1} (Fig. 3). Also the stretching CH vibrations increased in intensity. Extension of the equilibration time led to a coverage of all acid sites. The bands increased in intensity and shifted to 3615, 3209, 2785 and 1712, 1580 and 1482 cm^{-1}, respectively.

The spectra of methanol adsorbed on SAPO-5 at low pressure show a typical pattern of three doublets: a high frequency one above 3500 cm^{-1}, the second one consisting of broad bands at 2807 and 2473 cm^{-1}, and the third one below 1750 cm^{-1}. The two broad bands at 2807 and 2473 cm^{-1} have a similar height and half width. In accordance with the recent calculations [6,7], this is the so-called A-B-C pattern caused by a strong hydrogen bonding between methanol and Brønsted acid sites. However, no explanation can be given for the doublet at the highest frequency and for one low frequency deformation band. Another idea that protonated molecules may interact with the acid sites in two ways, *i.e.*, *via* OH or methyl group, is not probable considering both the ratio of intensities and the high intensity of the high frequency bands. From the IR data alone, it can not be decided which of the models is valid.

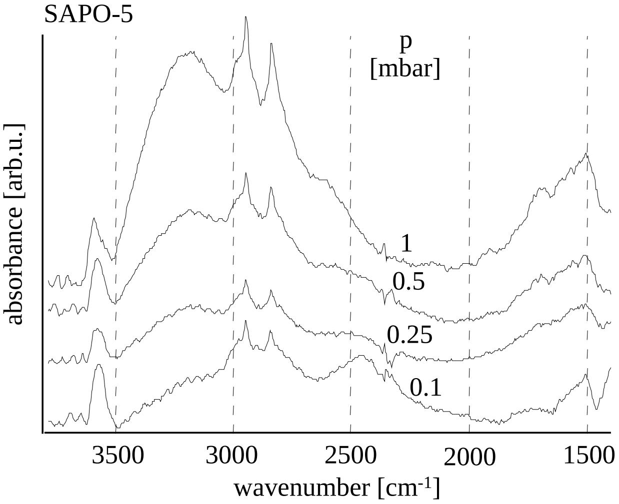


Fig. 3. Difference spectra between individual steps of the uptake of methanol in the pores of SAPO-5 single crystals.

At a higher pressure of methanol on SAPO-5, new bands arise at 3568, 2900, 2785, 1690 and 1525 cm^{-1}, attributed to methanol molecules strongly hydrogen bound to the acid sites located in two various channel systems. It is assumed that the band of v_{OH} vibration at around 3600 cm^{-1} contains at least two bands as can be concluded from both the shape and the fact that the band is cut on both sides by the negative absorption bands of the strong Brønsted acid sites. Methanol adsorbed in the large channels is reflected in the bands at 3568 (weakly perturbed v_{OH} of methanol), around 2900 (perturbed high frequency OH band) and 1525 cm^{-1} (bending OH band of methanol). Methanol molecules adsorbed on the strong acid sites in the narrow channels interact more strongly due to the space constraint [12]. This is reflected in the bands at 3568 (v_{OH} of methanol), 2785 (v_{OH} of perturbed low frequency OH), and 1690 cm^{-1} (OH bending of methanol). The reason for the different assignment of these bands as compared to those observed at the lowest pressure is a different intensity and half-width of the bands at 2900 and 2785 cm^{-1}. This is in agreement with the findings from experiments with methanol in the gas, liquid and solid phases [3,4] as well as with the common observation that stretching vibrations undergo a red shift with increasing interaction strength. In contrast, the deformation vibrations show the opposite trend. The broad band around 3100 cm^{-1} is assigned to the perturbed v_{OH} vibrations of methanol engaged into mutual hydrogen bonding. At a higher pressure, an over-proportional intensity increase occurs for the bands attributed to methanol interacting with the bridging OH groups and to hydrogen bound methanol. This intensity increase, occurring mainly for more weakly adsorbed methanol molecules, is followed by a blue shift of the bands originally located at 3568 and 3100 cm^{-1}.

The experiments leave open the question why two adsorption states of different interaction strength are observed for methanol (similarly to water [15]) on SAPO-5. At present, we may speculate that this is related to the formation of siliceous islands in the structure as described by Barthomeuf [16]. Such islands would create a zeolite-like environment and, since aluminium is less electronegative than silicon, the protonic strength should increase with the increasing number of silicon neighbours. Consequently, the strong Brønsted acid sites should be the preferred adsorption sites. This agrees well with the fact that these sites are covered before the regular bridging hydroxyl groups, which have only one silicon as neighbour. Note that previous results on single crystal samples with apolar compounds [12] did not indicate a distribution of acid strength of the bridging OH groups. Thus, we speculate that the bimodal distribution of strength is only seen for strongly polar molecules.

The temperature programmed desorption of methanol led to removal of all the adsorbed methanol molecules from $AlPO_4$-5 and SAPO-5 at around 550 and 730 K, respectively.

The adsorption/desorption cycles for all the single crystal samples measured did not lead to any changes of the spectra in relation to the unloaded molecular sieves. Therefore, it has been accepted that adsorption of methanol does not lead to changes in the structure of the $AlPO_4$-5 and SAPO-5 materials studied.

CONCLUSIONS

Adsorption of methanol on $AlPO_4$-5 reveals a weak coordinative interaction of methanol molecules with framework aluminium and a weak hydrogen bonding interaction with the terminal P-OH groups of the channels.

Small polar molecules of methanol adsorbed on the SAPO-5 single crystals reveal that two various surface species of the adsorbates occur. Both of them are bound *via* hydrogen bonds of different strength dependent on the adsorption sites. Interactions with the bridging hydroxyl groups are of the primary role. It is not clear why SAPO-5 exhibits bridging hydroxyl groups of different acid strength in relation to methanol, especially that the measurements with basic molecules [12] did not give evidence for a distribution of acid strength. The investigations also suggest that a single polar molecule adsorbed on a Brønsted site is hydrogen bound. A higher number of polar molecules enhances the interaction with the acid site by polarization of the primarily interacting molecule. SAPO-5 has shown IR bands of the adsorbed species at the lowest values of the adsorbate pressure. This indicates a higher adsorption affinity of SAPO-5, which is also supported by the higher desorption temperature as compared to $AlPO_4$-5 sample.

Interactions between the framework and the probe molecules in the narrow channels of both the $AlPO_4$-5 and SAPO-5 materials are stronger than in the large channels most likely due to the confined environment. Adsorption/desorption cycles of methanol does not lead to changes of framework structure of the single crystals.

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