In situ FT-IR microscopic investigation of metal substituted $\text{AlPO}_4\text{-5}$ single crystals

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Abstract

First direct spectroscopic evidence for the existence of Brønsted acid sites in $\text{AlPO}_4\text{-5}$ (AFI) single crystal molecular sieves substituted with divalent metal cations is reported. Ammonia and pyridine were used as probe molecules. Compared with unsubstituted $\text{AlPO}_4\text{-5}$ single crystals, the metal substituted samples exhibit well-developed bands of isolated hydroxyl groups and a broad absorption band indicating the existence of hydrogen bonded OH groups. Upon adsorption of pyridine on the metal substituted samples the formation of a new, relatively free vibrating hydroxyl group ($\nu_{\text{OH}} = 3690\text{--}3694\text{ cm}^{-1}$) was observed, giving evidence for a strong Lewis type interaction leading to the cleavage of a metal–oxygen bond close or at the position of the substituting metal cation. © 1997 Elsevier Science B.V.

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1. Introduction

The microporous aluminum phosphate $\text{AlPO}_4\text{-5}$ (AFI [1]) consists of regularly alternating AlO_4 and PO_4 tetrahedra creating an electrically neutral, but moderately polar framework. The lattice of $\text{AlPO}_4\text{-5}$ possesses a hexagonal symmetry and two parallel one-dimensional channel systems with 12 and 6 membered ring pore openings, respectively. The dominating acid sites are terminal P–OH and Al–OH groups with weakly Brønsted acidic character. In order to generate strong acid sites, isomorphous substitution of phosphorous with tetravalent metal cations (e.g.

Si^{4+}) or aluminum with divalent cations (e.g. Mg^{2+}) is necessary. However, for samples with divalent cations in the framework (such as magnesium and beryllium [2]), direct spectroscopic evidence for the presence of bridging hydroxyl groups (strong Brønsted acids) could not be given up to now. Thus, the present contribution focuses on in situ IR spectroscopic investigations of metal substituted $\text{AlPO}_4\text{-5}$ containing beryllium, magnesium and silicon in the framework, respectively. The goal of the contribution is to describe the acid sites of these materials and try to obtain direct IR spectroscopic information whether or not bridged hydroxyl groups in AFI type materials with aluminum partially substituted by bivalent cations exist.

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Table 1
Properties of the samples

Sample	Degree of substitution (at.%)	Sorption capacity at $p/p_s \approx 0.8$		Appearance and average dimensions (length $\times$ radius) (μm)	
		H ₂ O (mmol mg ⁻¹)	C ₆ H ₆ (mmol mg ⁻¹)		
AlPO ₄ -5		13.0	0.85	single	200 $\times$ 48
BeAPO-5 ^a	n.d.	n.d.	n.d.	twinned	320 $\times$ 22
MgAPO-5 ^b	4.42	13.5	1.48	single	150 $\times$ 32
SAPO-5	3.27	12.0	1.09	single	85 $\times$ 40

^a The crystals of these samples were obtained in a mixture with byproducts, which made a reliable bulk analysis impossible.

^b The values were determined for samples prepared by a parallel synthesis procedure with different metal sources; they are meant for orientation only.

2. Experimental

2.1. Material

For a detailed description of the synthesis of the AFI materials, see Refs. [3–6]. The Be²⁺ and Mg²⁺ substituted samples were calcined at 780 K for 36 h in air and for further 108 h in pure oxygen. AlPO₄-5 (SAPO-5) was activated for 144 h (216 h) in pure oxygen between 740 and 790 K. The characteristics of the samples used are compiled in Table 1.

2.2. Sorption experiments

Ammonia and pyridine were used as probe molecules. 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.

Before sorption, the calcined samples were heated in vacuum (10^{-6} mbar) with 10 K min^{-1} to 770 K (30 min) and then cooled with 10 K min^{-1} to 310 K. The sorbates were introduced into the reaction cell via a differentially pumped gas inlet system. The partial pressure (10^{-3} to 1 mbar) was held constant until sorption–desorption equilibrium was achieved. The sorption was followed in situ by time resolved FTIR microscopy (4 cm^{-1} spectral resolution).

3. Results

3.1. Activated samples

The spectra of all activated (template free) samples (given in Fig. 1) show bands in the region below

2500 cm^{-1} (2483sh (shoulder), 2371sh, 2352, 2231, 1972sh, 1845, 1790sh, 1662, 1603sh and 1450 cm^{-1}), which are assigned to overtone and combination vibrations of the lattice. In addition, absorption bands attributed to the stretching vibrations of hydroxyl groups are observed (see Table 2). AlPO₄-5 shows only one weak ν_{OH} band at 3672 cm^{-1} (attributed to the stretching vibration of terminal P–OH groups [7]).

Fig. 1. FT-IR spectra of activated, template free AFI single crystals.

Table 2
Infrared absorption bands for the activated samples

Sample	Position (cm ⁻¹)	Assigned to
AlPO ₄ -5	3672	terminal P–OH
BeAPO-5	3665	terminal P–OH
	3600	bridging Be–OH–P in large pores
	3520	bridging Be–OH–P in side rings
MgAPO-5	broad absorption (< 3600)	disturbed OH from extra lattice material
	3640, 3445	
SAPO-5	3735	terminal Si–OH
	3666	terminal P–OH or Al–OH
	3627	bridging Si–OH–Al in large pores
	3520	bridging Si–OH–Al in side rings

With SAPO-5, four absorption bands in the spectral region of the hydroxyl stretching vibrations are observed at 3735, 3666, 3627 (high frequency/HF-OH band) and 3520 cm⁻¹ (low frequency/LF-OH band). The latter two bands are assigned to bridging Si–OH–Al groups located in the 12 and 6 membered ring channels, respectively [4]. The lower wavenumber of the absorption maximum of the LF-OH band is caused by weak interactions of these hydroxyl groups with lattice oxygens in the narrow channels, which leads also to a broadening of the band. The band at 3735 cm⁻¹ is attributed to terminal Si–OH groups located at lattice imperfections inside the channels [8]; the band at 3666 cm⁻¹ stems either from terminal P–OH or Al–OH groups. The spectrum of BeAPO-5 shows a similar pattern as the SAPO-5 sample, but the position of the absorption maximum of the HF Be–OH–P group is shifted to lower wavenumbers (3600 instead of 3627 cm⁻¹). MgAPO-5 has a broad band with the absorption maximum below 3600 cm⁻¹. This band is assigned to hydrogen bonded hydroxyl groups attached to extra lattice material. Additional maxima are found in the region between 3476 and 3640 cm⁻¹. They might originate from bridged hydroxyl groups, but an unequivocal assignment cannot be given at this state of the investigation.

3.2. Sorption of ammonia

Generally, the uptake of ammonia was very slow. Ammonia adsorbed at a partial pressure of 10⁻¹ mbar on AlPO₄-5 leads to a full coverage of the P–OH groups. The difference spectrum (Fig. 2) shows a

negative IR band (corresponding to a decrease in intensity upon sorption) at 3672 cm⁻¹ ($\nu_{\text{P-OH}}$) and broad positive bands (corresponding to an increase in intensity upon sorption) at 3379 and 3284 cm⁻¹ (ν_{NH}). Increasing the equilibration time and pressure

absorbance [arb. units]

Fig. 2. Difference spectra of ammonia sorbed on: (a) AlPO₄-5; (b) BeAPO-5; (c) MgAPO-5; (d) SAPO-5.

causes new, continuously growing sharp IR bands at 3395, 3302 (ν_{NH}) and 1616 cm^{-1} (δ_{NH}). Because all the P–OH groups are covered at this time, these bands can be exclusively ascribed to Lewis bound ammonia.

The difference spectra of ammonia sorbed on SAPO-5 (Fig. 2) at a coverage of the strong Brønsted acid sites (Si–OH–A) of $\Theta = 0.3$ (0.1 mbar) shows negative peaks at 3627 and 3520 cm^{-1} (Si–OH–Al groups) and positive bands at 3366, 3256, 2680, 1923 and 1450 cm^{-1} (the latter being characteristic for protonated ammonia) and 1620 cm^{-1} (attributed to Lewis bound ammonia). At a coverage of the bridged hydroxyl groups of $\Theta = 1$ (0.1 mbar) a new band at 2926 (shoulder) was observed and the ν_{NH} bands shifted to higher wavenumbers (3373 and 3278 cm^{-1}). This can be explained by the increased fraction of ammonia sorbing on Lewis acid sites. Changing the pressure to 1 mbar leads to an increase in intensity of all bands typical for Lewis bound ammonia. With BeAPO-5 we observed at 10^{-2} mbar only Brønsted type interaction, the difference spectrum (Fig. 2) shows negative bands at 3600 and at around 3520 cm^{-1} (ν_{OH}) and positive bands at 3392, 3272 (ν_{NH}) and 1456 cm^{-1} (δ_{NH} , characteristic for protonated ammonia). After increasing the pressure we also observed the δ_{NH} absorption band of NH_3 typical for coordinatively bound ammonia at 1615 cm^{-1} , the ν_{NH} bands shifting due to this interaction upwards to 3401 and 3302 cm^{-1} , respectively. The difference spectra of ammonia sorbed on MgAPO-5 (Fig. 2) show 3 negative maxima at around 3660, 3630 and 3512 cm^{-1} , the latter two assigned to the respective Mg–OH–P groups in the large and small channel system, respectively. The two shoulders of the band at 3512 cm^{-1} are attributed to IR interference patterns in the spectra caused by the reflections from crystal terminating planes.

3.3. Sorption of pyridine

The spectrum of pyridine sorbed on $\text{AlPO}_4\text{-5}$ (Fig. 3) shows only absorption bands typical for coordinatively bound pyridine. The IR bands between 3200 and 3000 cm^{-1} are attributed to the CH stretching vibrations of pyridine; the bands in the low frequency region with the maxima at 1609, 1577, 1494 and 1447 cm^{-1} are characteristic vibrations of Lewis bound pyridine to Al^{3+} [9].

Fig. 3. Difference spectra of pyridine adsorbed at 1 mbar on: (a) $\text{AlPO}_4\text{-5}$; (b) BeAPO-5 ; (c) MgAPO-5 ; (d) SAPO-5 .

The difference spectrum of pyridine sorbed on SAPO-5 (Fig. 3) shows absorption bands typical for both, Lewis and Brønsted bound pyridine, negative bands of the bridging Si–OH–Al (3627, 3520 cm^{-1}) groups and the P–OH groups (3673 cm^{-1}). The bands characteristic only for protonated pyridine are located at 1634 and 1547 cm^{-1} . A new IR absorption band appears upon sorption of pyridine on SAPO-5 at 3694 cm^{-1} .

With BeAPO-5, all Brønsted acid sites are equilibrated with 10^{-3} mbar pyridine. The difference spectrum shows negative absorption bands at 3600 and 3520 cm^{-1} (due to a decrease in intensity of the bands of the bridged hydroxyl groups) and bands at 1541, 1489 and 1447 cm^{-1} attributed to protonated pyridine. After increasing the pressure to 10^{-2} mbar, absorption bands typical for Lewis bound pyridine rise at 1610 and 1578 cm^{-1} . While these bands further increase in intensity with increasing equilibration time and pressure, a new band around 3690 cm^{-1}

appears (see Fig. 3), similar to the band observed upon sorption of pyridine on SAPO-5.

With MgAPO-5, we observe only Lewis bound pyridine and protonation of pyridine did not occur. However, after equilibration with 1 mbar pyridine we again observe the new absorption band situated around 3690 cm^{-1} (Fig. 3).

4. Discussion

Ammonia shows a Lewis type interaction with the lattice of single crystals investigated. This interaction takes place between the lone electron pair of ammonia and the metal atoms of the lattice. Kustanovich et al. [10] found a change in the coordination number of aluminum in $\text{AlPO}_4\text{-5}$ from 4 to 6 upon sorption of ammonia by using NMR techniques. The same kind of interaction also takes place between pyridine and the lattice of the AFI samples. The model of the change in the coordination number of the metal cation upon sorption of the probe molecule is supported by the position of the absorption band characteristic for coordinatively bound pyridine around 1610 cm^{-1} , which is according to Pohle and Fink [9] characteristic for an octahedral coordination.

The position of the ammonia absorption bands was comparable for all investigated metal substituted molecular sieves—only the rate of uptake on the Lewis acid sites differed. For SAPO-5, the rate of sorption on the Lewis acid sites was slower than that on the Brønsted acid sites. After full coverage of the Brønsted acid sites, the rate of uptake of the Lewis acid sites increased. In the case of BeAPO-5, first all Brønsted acid sites were covered, in the case of MgAPO-5, the two processes occurred in parallel. Compared to the rate of uptake on the hydroxyl groups, the relative rate of sorption on the Lewis acid sites decreased in the order $\text{Mg} > \text{Si} > \text{Be}$. A similar behavior was found with pyridine, where we observed only Lewis type interaction with the substituted sample (Mg), a parallel uptake on both Lewis and Brønsted acid sites for SAPO-5 and a highly preferential adsorption on the Brønsted acid sites in the case of BeAPO-5. This suggests that the strength of sites capable to coordinatively sorb ammonia decreases in the sequence mentioned.

One spectral feature all substituted samples have in

Fig. 4. Proposed interaction between pyridine and metal cation generating the free vibrating OH group.

common is a broad absorption band below 3500 cm^{-1} , which did not disappear upon sorption of ammonia or pyridine. We suggest that this band stems from hydrogen bonded hydroxyl groups either from extra lattice material or from lattice defects inaccessible to the probe molecules. Because this feature does not appear in $\text{AlPO}_4\text{-5}$, we believe that the incorporation of the cations leads to a partial destruction of the framework. This can also explain the lower accessibility for pyridine observed with these samples. The relative intensity of the absorption bands of pyridine compared to the intensity of the lattice vibrations indicates that the pore system of MgAPO-5 single crystals is almost inaccessible for pyridine.

The new absorption band observed upon sorption of pyridine on the substituted samples around 3690 cm^{-1} is observed for the first time in metal substituted aluminum phosphates. The intensity of this band grows in parallel with the intensity of the bands characteristic for coordinatively bonded pyridine. Thus, we assume that through a strong coordinative interaction of the lone electron pair of pyridine with the metal cation, the bond between the cation and the neighboring oxygen is broken, creating a relatively free vibrating (based on the high wavenumber and sharpness of the band) hydroxyl group (see Fig. 4 for the case of a divalent metal cation).

5. Conclusions

1. The substitution of either P or Al by tetra- or divalent cations led to the formation of bridging hydroxyl groups in both channel systems of the AFI structure.
2. With the present single crystals (SAPO-5, BeAPO-5 and MgAPO-5), as a side effect of the implementation of the metal cations into framework positions, the accessibility of the pore systems

decreased for the larger pyridine molecules. Speculatively this is attributed to the deposition of extra lattice material in the pores and/or to partial destruction of the framework. The existence of a broad absorption band of hydrogen bonded hydroxyl groups, which are inaccessible for the probe molecules, supports this model.

3. The strong coordinative interaction of pyridine with the metal cations leads probably to the cleavage of metal–oxygen bond of the lattice by forming a relatively free vibrating new hydroxyl group ($\nu_{\text{OH}} = 3690\text{--}3694\text{ cm}^{-1}$).

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