STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLVII, 1-2, 2002

Dedicated to Professor Ionel Haiduc
on the occasion of his 65th birthday

ADSORPTION OF AMMONIA AND PYRIDINE ON CoAPO-5 SINGLE CRYSTALS STUDIED BY *IN SITU* FT-IR MICRO-SPECTROSCOPY

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ABSTRACT. Direct spectroscopic evidence for the existence of Brønsted acid sites in CoAPO-5 single crystal molecular sieves is reported. Compared with unsubstituted $AlPO_4$-5 single crystals, the cobalt substituted samples exhibit well developed bands of isolated bridging hydroxyl groups and a broad absorption band indicating the existence of hydrogen bonded OH groups. Ammonia and pyridine interact with the bridging OH groups. This seems to involve simultaneous interactions with Lewis and Brønsted acid sites. Upon adsorption of pyridine new hydroxyl groups (ν_{OH} = 3682 and 3590 cm^{-1}) were observed in parallel to pyridine bonding to Lewis acid sites. This suggests opening framework metal-oxygen bonds during sorption of pyridine.

Keywords: Cobalt substituted AFI; Single crystals; FT-IR spectroscopy

INTRODUCTION

$AlPO_4$-5 (AFI framework type structure [1,2]) has hexagonal symmetry and contains two parallel one-dimensional channels formed by 12-, and 6-membered rings (see Fig.1a) composed of alternating AlO_4 and PO_4 tetrahedra creating an electrically neutral framework. The larger channels allow sorption of molecules as large as 2,2-dimethylpropane (0.62 nm) [2]. The dominating acid sites observed 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 cations (e.g., Si^{4+}, reported first by Lok *et al* [3]) or aluminum with divalent cations (e.g., Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Zn^{2+} [4], Co^{2+} [5]) were performed. Flanigen *et al* [6] reported incorporation of several metal cations leading to combinations of up to six framework cations.

However, direct spectroscopic evidence for the presence of bridging hydroxyl groups (strong Brønsted acids) is scarce for samples with divalent metal cations in the framework. Recent studies by FT-IR microscopy of some metal substituted single crystals [7] showed that upon sorption of pyridine on bridging hydroxyl groups of SAPO-5, BeAPO-5, MgAPO-5 and CoAPO-5, a new hydroxyl group (ν_{OH} = 3690-3694 cm^{-1}) was formed in parallel to the coordination of pyridine to a strong Lewis acid site. This was interpreted as pyridine cleaving the bond between the oxygen and the metal cation of the bridging OH group [7].

Among the metal substituted aluminophosphate molecular sieves the cobalt substituted ones are the most studied [5, 8-27]. The introduction of a transition metal cation possibly creates redox properties which makes CoAPO a potential catalyst for acid-catalyzed and redox type reactions [5,8-12,15,18,22]. However, the nature of the site allowing the valence change in redox reactions is not defined and the reports are controversial. Bridging OH groups, the direct evidence of Co^{2+} in the framework, could not be found by IR spectroscopy of polycrystalline materials [10,11,15,22]. The present contribution describes an FT-IR micro-spectroscopic study to overcome some of the ambiguities in the characterization of CoAPO-5 by studying large well-defined crystals.

EXPERIMENTAL

For a detailed description of the synthesis of CoAPO-5 see [27]. The crystals were calcined at 780 K for 36 hours in synthetic air and subsequently 108 hours in pure oxygen. The single crystals (Fig.1b) used had a degree of substitution: 2.07 atom%, sorption capacities (at p/ps = 0.8): 13.5 mmol H_2O/mg, 1.19 mmol C_6H_6/mg; average dimensions: 290x40 µm.

Ammonia (99.998%, Union Carbide) and pyridine (99.8%, ALDRICH) were used as probe molecules. The experiments were carried out in a vacuum cell equipped with i.r. transparent windows which was attached to the stage of a BRUKER i.r. microscope coupled to a BRUKER IFS 88 spectrometer.

The externally calcined crystals were introduced in the i.r. cell and heated in vacuum (10^{-6} mbar) or in hydrogen flow (40 cm^3/min) with 10 K/min to 770 K (60 minutes). After cooling in vacuum (10 K/min) to 310 K, spectra of selected crystals were recorded. The sorbates were introduced into the i.r. 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 FTIR micro-spectroscopy (1000 scans/spectrum 4 minutes, 4 cm^{-1} spectral resolution). Subsequently, the cell was evacuated (p = 10^{-6} mbar, T = 310 K) and the temperature was increased with 10 K/min to 870 K.

RESULTS AND DISCUSSION

Activated Crystals

The spectra of the crystals activated in vacuum and in hydrogen flow are identical and show bands (Fig.1c) attributed to the stretching vibrations of hydroxyl groups. The absorption band at 3655 cm^{-1} is attributed to OH stretching vibrations of terminal P-OH, Al-OH and/or Co-OH groups, respectively. This assumption is based on analog observations made with other MAPOs [7]. If only free terminal P-OH groups were present, the absorption band should be positioned at around 3670 cm^{-1}.

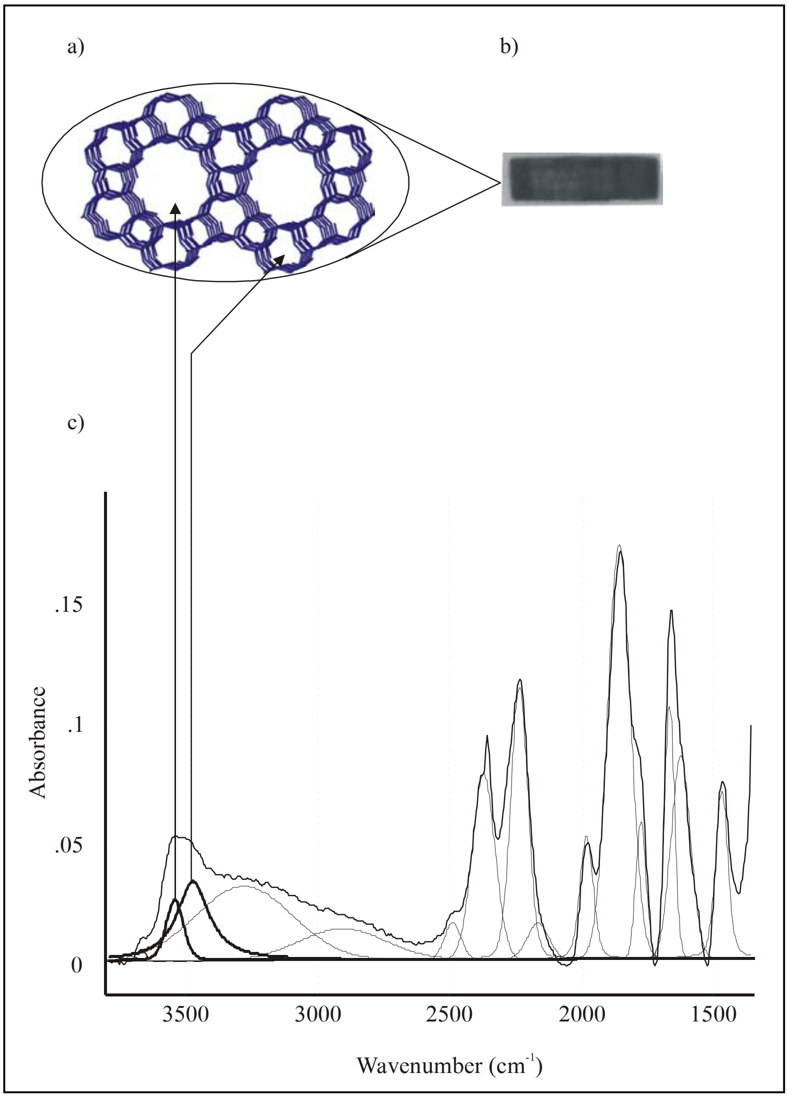

Fig.1: a) Channel systems of AFI, reproduced from the BIOSYM molecular modelling software; b) Optical micrograph of the sample; c) FT-IR spectrum of activated, template free CoAPO-5 single crystal (T = 310 K, p = 10^{-6} mbar)

In analogy to SAPO-5 [7], the band at 3540 cm^{-1} is assigned to the stretching vibrations of bridging OH (Co-OH-P) groups situated in the 12 membered channels, and the band at 3470 cm^{-1} to bridging OH groups in the 6 membered channel system. The presence of bridging OH groups suggests that the activated crystals contain the cobalt ions mainly in the form of Co^{2+}. Even when the calcination was carried out in pure oxygen, the main part of the framework cobalt remained at that oxidation stage, in agreement with the recent observations on a polycrystalline CoAPO-5 [21]. Further activation in hydrogen flow does not produce a change in the spectral feature, indicating that the extant framework Co^{3+} is not reduced by hydrogen to Co^{2+} even at 770 K. The broad absorption band below 3450 cm^{-1} was assigned to hydrogen bonded hydroxyl groups affiliated with the presence of some debris in the crystal because the absorption band was not affected by any of the molecules adsorbed. In addition, bands were observed in the region below 2500 cm^{-1} (2483shoulder/sh, 2371sh, 2352, 2227, 1975, 1845, 1790sh, 1662, 1603sh, 1450 and 1268 cm^{-1}), which are assigned to overtone and combination vibrations of the lattice.

Sorption of ammonia and pyridine

Ammonia - The difference spectra of adsorbed ammonia (Fig. 2) showed negative i.r. absorption bands in the region of the OH stretching vibrations at 3551 and around 3487 cm^{-1} attributed to the decreasing in intensity of the bridging OH stretching vibrations resulting from the interaction of Co-OH-P groups with ammonia. Increasing equilibration time led to a new asymmetric negative band at around 3655 cm^{-1}, caused probably by the sorption of ammonia on terminal P-OH and Co-OH groups. NH stretching vibrations were detected at 3394, 3284, 3224 and 3190 cm^{-1}. The respective maxima for the NH deformation vibrations were found at 1665, 1618 (assigned to coordinatively bonded ammonia) and at 1445 with a shoulder at 1486 cm^{-1} (assigned to protonated ammonia) [29]. Increasing equilibration time (and hence the coverage), the NH stretching vibrations shifted to lower wavenumbers. Another difference appeared by subtracting the spectrum equilibrated at 10^{-3} mbar with a spectrum at an earlier stage of uptake (Fig. 2). At lower uptake, the two δ_{NH} bands assigned to protonated ammonia had equal intensity, whereas the low frequency δ_{NH} band grew over proportionally with increasing time. Furthermore, two broad absorption bands are observed with their maxima around 2925 and 2723 cm^{-1}, which are assigned to NH stretching vibrations of ammonium ions interacting with the lattice oxygen [30].

Increasing the pressure to 10^{-2} mbar showed only a subtle change in the spectral features of adsorbed ammonia (see Fig. 2). Three bands were observed in the NH stretching region at 3362, 3285 with a shoulder at 3200 cm^{-1}. We did not detect negative bands in the hydroxyl stretching vibration region. This suggests that the accessible acid sites were already completely covered at 10^{-3} mbar. Further increase in pressure led probably to a clustering of ammonia molecules, as indicated by an over proportional growth of the bands at 3362 (ν_{NH}) and at 2750 cm^{-1} (ν_{NH} perturbed by ammonia-ammonia interaction). The final pressure step to 1 mbar caused the appearance of sharp bands of physisorbed ammonia at 3400, 3343, 3302 (ν_{NH}) and 1616 cm^{-1} (δ_{NH}). The relatively broad absorption band with the maximum at 2755 cm^{-1} is attributed to the perturbed NH stretching vibrations of physisorbed ammonia (hydrogen bonding ammonia-ammonia interactions).

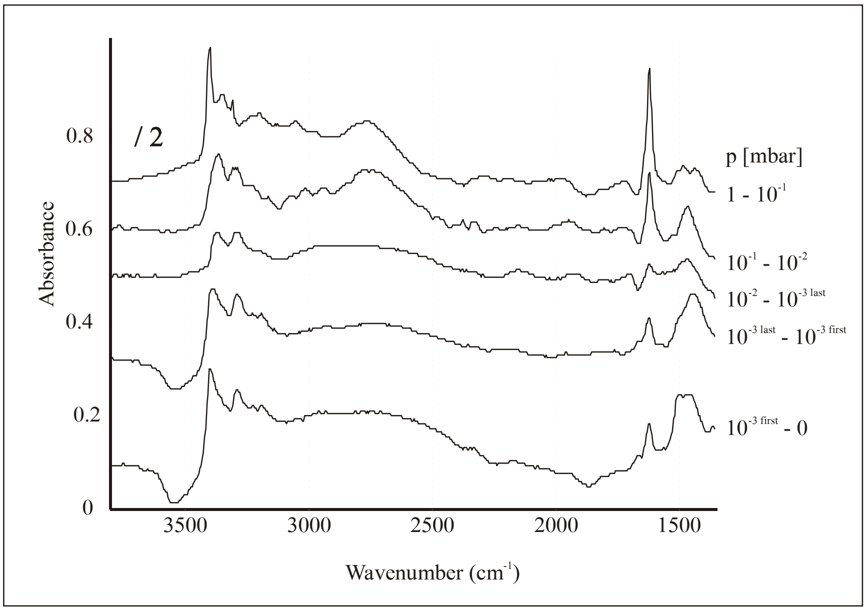

Fig. 2. Difference spectra of ammonia adsorbed on CoAPO-5 at the indicated pressures, T=310 K.

The sorption of ammonia led at low pressures to two pairs of δ_{NH} i.r. absorption bands assigned to coordinatively bonded (1665 and 1618 cm^{-1}) and to protonated molecules (1486 and 1445 cm^{-1}), respectively. We tentatively attribute the high frequency bands of the pairs to ammonia interacting with the acid sites in the constraint environment of the 6-membered pores. Note, that the low frequency bands of these two pairs rose faster in intensity with increasing pressure and equilibration time than the high frequency bands. We speculate this to be caused by the faster transport of ammonia in the large channels compared to the small pore channels.

Because the i.r. absorption bands characteristic for both Lewis bound and protonated ammonia rose in parallel, we suggest that two ammonia molecules are adsorbed per Co-OH-P unit. The first molecule forms a strong coordinative interaction with the cobalt ion, giving rise to the bands close to 1600 cm^{-1}, opening the metal oxygen bond creating a new P-OH group [21]. The proton of the P-OH group is transferred to the second ammonia molecule causing the bands close to 1450 cm^{-1}.

Despite the fact that at 10^{-3} mbar all Brønsted acid sites were covered we still detected absorption bands for both coordinatively bonded and protonated species suggesting a certain mobility of the proton detached from the Brønsted acid sites within the ammonia clusters formed at higher partial pressures.

Evacuation of the system to 10^{-6} mbar led to the desorption of all physisorbed species. The spectrum was comparable to the spectrum of the crystal equilibrated with 10^{-2} mbar of ammonia (see Fig. 2). During TPD the desorption of ammonia molecules began at around 510 K, and was completed at 710 K. The spectra of the crystal before and after undergoing the experimental procedures were identical.

Pyridine - The strong Brønsted acid sites (Co-OH-P) reach their maximum coverage (approximately a third of the acid sites, estimated from the decrease of the hydroxyl stretching vibrations) at 10^{-2} mbar (Fig. 3). Up to this pressure all absorption bands grew continuously in intensity. Negative bands appeared at 3538 and 3485 cm^{-1}, which are assigned to the stretching vibrations of the strong acidic bridging OH groups interacting with pyridine. The spectral region between 1650 and 1350 cm^{-1} typically used to characterize the adsorption state of pyridine showed the characteristic bands for both coordinatively bonded pyridine to the framework cobalt (1610 and 1449 cm^{-1}) and protonated pyridine (1635 and 1544 cm^{-1}). The presence of protonated pyridine is supported by the absorption bands at 3393 and 3279 cm^{-1} too, which are assigned to ν_{NH} vibrations. The broad band at around 2765 cm^{-1} is assigned to perturbed NH stretching vibrations (i.e., red shifted through interactions with the lattice oxygen atoms).

By increasing the pressure to 10^{-1} mbar (Fig. 3) new i.r. absorption bands appeared at 3682 and 3590 cm^{-1} with an underlying broad absorption band centered around 3180 cm^{-1}. This broad feature is interrupted by negative bands at 3538 and 3485 cm^{-1} of the bridging OH groups involved in the interaction with pyridine. The two new absorption bands at higher wavenumbers (3682 and 3590 cm^{-1}) are assigned to relatively free vibrating hydroxyl groups. In the low wavenumber region the i.r. bands characteristic for coordinatively bound (1610 cm^{-1}) and hydrogen bonded (1576 cm^{-1}) pyridine increased stronger than the absorption band assigned to protonated pyridine. The spectrum at 1 mbar pyridine pressure shows a marginal increase of all bands already observed at 10^{-1} mbar.

Upon evacuation of the system the bands at 1608, 1576 and 1446 cm^{-1} (attributed to physisorbed pyridine) decreased in intensity (Fig. 3). During TPD the i.r. bands of the newly formed hydroxyl groups disappeared around 510 K, whereas desorption of chemisorbed pyridine on Brønsted and Lewis sites was not observed before 550 K. Both protonated and coordinatively bound pyridine were completely removed at 870 K.

With pyridine the interactions are similar to those of the ammonia. Up to a partial pressure of 10^{-2} mbar two pyridine molecules interact per acid site, breaking the cobalt-oxygen bond creating a relatively free vibrating P-OH group which is deprotonated by the second pyridine molecule. This model is supported by the fact, that the absorption bands characteristic for the two different pyridine species rose in parallel. At higher partial pressure two new i.r. bands appeared at 3682 and 3590 cm^{-1}. We suggest that under these conditions the remaining void space does not allow for the pyridine P-OH interaction. These bands are assigned to the P-OH groups created due to the strong coordinative interaction of pyridine leading to the opening of the metal oxygen bond. The appearance of two bands is explained again by the two possible positions of the Co-OH-P units in the crystal structure (the high frequency band originating from the acid sites in the 12-membered ring channels and the low frequency band stemming from the sites in the 6-membered ring channels).

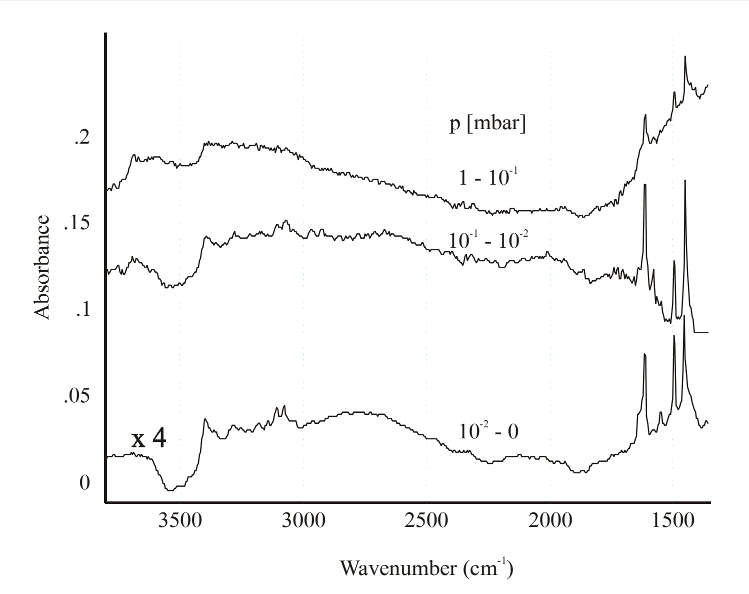

Fig. 3. Difference spectra of pyridine adsorbed on CoAPO-5 at the indicated pressures, T=310 K.

The broad underlying absorption band (3180 cm^{-1}) might be caused by a very weak interaction of some of the newly formed P-OH groups involved in hydrogen bonding to pyridine molecules. This explains also the absorption band characteristic for hydrogen bonded pyridine at 1576 cm^{-1}. The assumption that the appearance of free vibrating P-OH is caused by a steric hindrance at higher partial pressures is supported by the fact that at first upon evacuation and consecutive temperature programmed desorption of pyridine (hence a decrease in the amount of adsorbed pyridine) up to 510 K only the absorption bands characteristic for the newly formed free P-OH groups decreased. The characteristic bands of chemisorbed species (protonated and Lewis bonded) did not decrease in intensity before 550 K.

In the course of pyridine sorption/desorption the intensity of the broad i.r. band ascribed to hydrogen bonded hydroxyl groups attached to extra lattice material decreased. This indicates that some of this material was removed due to experimental procedures.

The spectra of CoAPO-5 recorded before and after the experimental procedures with pyridine was identical with the exception of a decrease of the intensity of the broad absorption band (3000-3450 cm^{-1}) attributed to the hydrogen bonded OH groups attached to extra lattice material.

CONCLUSIONS

CoAPO-5 single crystals contain Brønsted acid sites in both 12-membered and 6-membered channel systems. Even if the calcination of crystals is carried out in air and oxygen, the FT-IR spectra contain the characteristic bands of bridging OH groups suggesting that the main part of framework cobalt ions remain as Co^{2+}.

The adsorption of ammonia and pyridine on CoAPO-5 samples gives proof for the existence of both Brønsted and Lewis acid sites. Due to the parallel increase of the intensity of the respective characteristic IR bands we suggest an adsorption mechanism with two probe molecules interacting with one Co-OH-P unit. The first molecule forms a strong coordinative bond to the cobalt ion and cleaves the metal-oxygen bond creating a P-OH group which binds the second base molecule.

Upon adsorption of pyridine at higher loadings two new, relatively free vibrating P-OH groups (ν_{OH} = 3682 and 3590 cm^{-1}) are formed, the sterical hindrance preventing the interaction of a second pyridine molecule with the newly formed OH groups. In opposite to ammonia, pyridine was unable to access all the Brønsted acid sites; extra framework material deposited in the channel system blocks parts of it for larger molecules.

ACKNOWLEDGEMENT

The financial support of the Christian Doppler Laboratories is greatly appreciated.

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