In Situ Infrared Study of SBA-15 Functionalized with Carboxylic Groups Incorporated by a Co-condensation Route

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Two samples of SBA-15 mesoporous silica with a different content of carboxylic groups (−COOH) were prepared by a co-condensation route, using 4-(triethoxysilil)butyronitrile as the organosilane agent, then treating the samples with sulfuric acid, which removes the template and simultaneously hydrolyses the −CN to −COOH groups, as shown by IR spectroscopy. Both incorporation of organosilane agents and subsequent acid treatment do not affect the ordered SBA-15 structure. The proton-donor ability of carboxylic groups, as well their accessibility to reactants, has been studied in the IR by dosing ammonia, which forms reversibly COO^- groups and NH_4^+ ions. The related equilibrium constants have been determined by elaboration of IR data. Outgassing the samples at progressively increasing temperatures destabilizes to an increasing extent the ammonium/carboxylate ion pair, because of the decrease in surface polarity brought about by dehydration: this decreases the related equilibrium constants. The amount of carboxylic groups undergoing reaction appears instead to be constant with dehydration, and to coincide with the whole population of COOH groups. Titration with alkali solutions yielded surface concentrations for the two samples of ca. 1.0 and 0.45 $COOH/nm^2$. Proportionality between the surface concentrations and the intensities of the C=O IR band is observed: this suggests that COOH groups are noninteracting with each other and allows the computation of the related extinction molar coefficient.

Introduction

Surface tailoring of ordered mesoporous silica-based materials is a promising method for the synthesis of organic−inorganic hybrid materials, which combine into a single solid the structural properties of the rigid inorganic lattice and the chemical reactivity of the organic components.[1−4] Such materials are candidates for applications such as catalysis,[5−6] separation,[7] adsorption of heavy metals,[8] chemical sensing and immobilization of biomolecules.[9]

Two approaches to surface tailoring are possible, i.e., post-modification (grafting of suitable molecules at the surface of already prepared mesoporous silica), and co-condensation in a sol−gel synthesis of a tetra-alkoxysilane and an organo-alkoxysilane in the presence of surfactant template. The two routes lead to different distribution of functional groups[10] and to different accessibility and reactivity.[9] Therefore, a characterization of the nature, accessibility, and reactivity of anchored functionalities is vital to understand the performance of these hybrid systems.

Reactivity of different organic groups within mesoporous silica has been basically studied via metal-ion binding at these sites.[11] Such studies provide information on the availability of the active sites and the rate of access to them, but allow only an indirect characterization of the functional group population. In our opinion, in situ infrared spectroscopy concerning the interaction of probe molecules with active sites provides an appropriate tool to investigate the surface chemistry of functionalized materials.[12]

The present paper reports the IR characterization of a −COOH-functionalized SBA-15 mesoporous silica prepared via co-condensation by means of an in-situ study of the interaction with ammonia.

Experimental Section

Preparation of SBA-15 functionalized with −COOH groups involves a one-pot synthesis of cyanide-functionalized hybrid material followed by treatment with sulfuric acid. Pluronic P123 triblock copolymer ($EO_{20}-PO_{70}-EO_{20}$, BASF) was used as surfactant: this was dissolved into a hydrochloric acid solution at 313 K, then 4-(triethoxysilyl)butyronitrile, $(EtO)_3Si-BuCN$ (98%, Aldrich), was introduced together with tetraethylorthosilicate, (TEOS, 98%, Aldrich), and the mixture was stirred for 24 h. The mixture was then transferred to a Teflon bottle and heated at 373 K for 2 days. The molar composition of the gel was

$$(1-x) \text{ TEOS} : 0.017 \text{ P123} : 2.9 \text{ HCl} : 202.6 \text{ H}_2\text{O} : x(\text{EtO})_3\text{Si}-\text{BuCN}$$
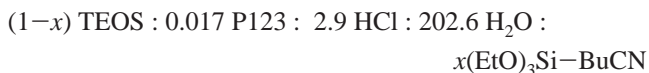
Two samples were prepared with $x = 0.07$ and 0.10, referred to hereafter as 7-COOH−SBA-15 and 10-COOH−SBA-15, respectively. The products were filtered, washed with water, and dried at 363 K. To remove the template and to hydrolyze the −CN groups, the procedure reported by Schüth et al.[13] was followed: 1.0 g dried sample was re-dispersed in 120 mL of 48% H_2SO_4 solution, and the mixture was heated to 368 K for 1 day. The product was washed with water until the eluent became neutral, then washed with acetone.

The samples were characterized by powder X-ray diffraction (Philips X'pert, Cu Kα radiation). Nitrogen adsorption−desorption measurements were conducted at 77 K on a Micromeritics ASAP2000 sorptometer. BET specific surface area were calculated in the relative pressure range 0.04−0.1. The

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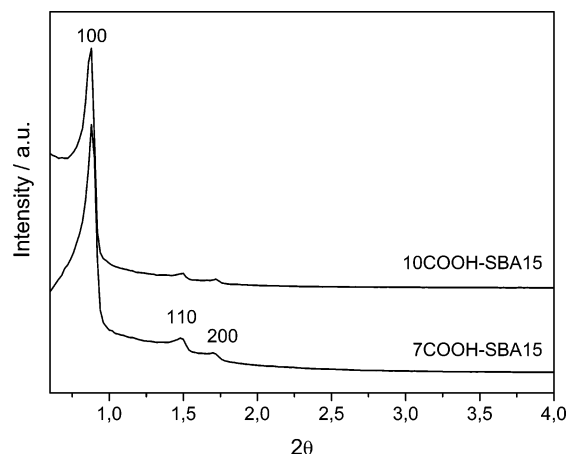
Figure 1. X-ray diffraction patterns of 7-COOH−SBA-15 and 10-COOH−SBA-15.

Figure 2. Adsorption isotherms of nitrogen at 77 K concerning the two samples 7-COOH−SBA-15 (curve a) and 10-COOH−SBA-15 (curve b).

TABLE 1: Textural Properties of −COOH Functionalized Samples

sample	surface area (m^2/g^{-1})	pore diameter (nm)
7-COOH−SBA-15	588	9.2
10-COOH−SBA-15	522	8.9

pore size diameter was calculated using the BdB method for the desorption branch.

Thermogravimetric (TG) analyses were carried out on a Mettler Toledo thermogravimetric analyzer with a heating speed of 10 K/min under air in a flow of 50 mL/min.

The −COOH concentration has been estimated by titration with diluite sodium hydroxide solution.

For FTIR measurements, the powder was pressed into thin self-supporting wafers, which were placed into a quartz cell and activated for 2 h under dynamic vacuum (residual pressure < 10^{-3} mbar) at several temperatures in the range room-temperature to 673 K. Ammonia was dosed in the pressure range from 0.1 to 100 mbar, by connecting the IR cell to a vacuum frame (residual pressure < 10^{-3} mbar). Spectra were recorded using a Bruker Equinox 55 spectrometer operating at 2 cm^{-1} resolution.

Results and Discussion

Figure 1 reports the XRD pattern of the acid-treated samples 7-COOH−SBA-15 and 10-COOH−SBA-15. Both samples show a highly ordered hexagonal structure, indicating that the incorporation of increasing amounts of functional groups and the acid sulfuric treatment do not affect the order. No change is observed in the position of the reflections with increasing population of functional groups: the cell parameter, as calculated from the position of the (100) peak reflection, is 11.6 nm in both cases.

The two samples show nitrogen sorption isotherms characterized by a sharp step with hysteresis loop corresponding to the filling of the ordered mesopores (Figure 2). Corresponding specific surface areas and average pore size are reported in Table 1. Both samples have large pores and high surface area: both features decrease, however, with increasing amount of organoalkoxysilane, notwithstanding the constancy of the cell parameter, because of the lining of the internal wall by the organic groups.

Microporosity of the samples was investigated by examining the low-pressure portion of the isotherm by a *t*-plot with an empirical Harkins-Jura equation. *t*-Plot curves (not reported) for both samples gave a straight line between *t* = 4 Å and *t* = 8 Å: the extrapolation line intercepts the *y*-axis very close to the origin, indicating that there is nearly no microporosity in the systems. This agrees with the data by Schüth,[14] who ascribed the absence of microporosity to residual ethylene oxide units occluded in the micropores, and thus not able to react with H_2SO_4.
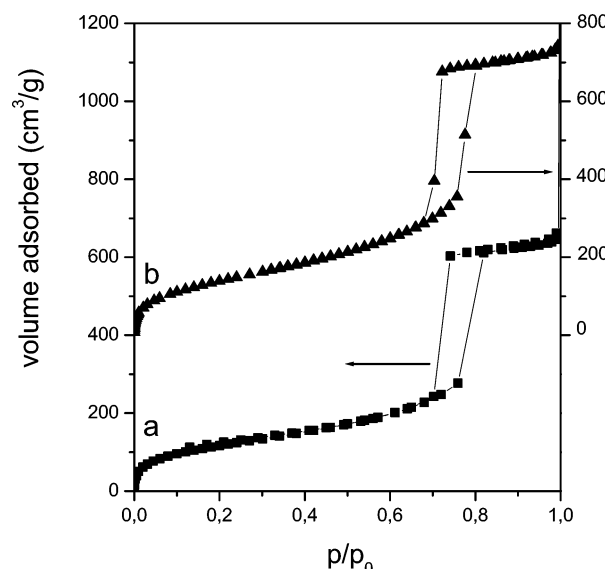
TG analyses of both samples show small weight losses at temperature below 370 K (release of adsorbed water), in the range 430−520 K (decomposition of residual copolymer surfactant), and a more significant weight loss between 670 and 870 K, ascribable to the decomposition of the carboxybutyl groups.

The −COOH concentration for the sample 10-COOH−SBA-15 estimated by titration was ca. 0.9 mmol g^{-1}, that for the sample 7-COOH−SBA-15 0.50 mmol g^{-1}. If all the functional groups are assumed to be located on the surface, the surface density of −COOH group is ca. 1.0 nm^2 and 0.45 nm^2. The weight loss as measured by TG is in fair agreement with these values.

Infrared Spectroscopy Measurements. Curve a in Figure 3, is the IR spectrum of the as-prepared, template-bearing 7-COOH−SBA-15 sample outgassed at room temperature. This shows in the region 2950−2850 cm^{-1} very intense C−H stretching bands due to hydrocarbon chains of the template. Their strong decrease, observed with the acid-treated sample (spectrum b), witnesses template removal. The weak band at 2965 cm^{-1}, due to a CH_3 stretching mode, may indicate the presence of residual small amounts of template, in particular that filling the micropores, as discussed above, which also contribute to the bands at 2942 and 2879 cm^{-1} (−CH_2 stretching modes). These latter absorptions may also be due to the butyl chains of the functional groups: the ratios of intensities of the three bands are indeed different in spectra a and b.

The inset reports the magnification of the region 1500−2300 cm^{-1}: spectrum a shows a band at 2247 cm^{-1} due to the −CN stretch, and two bands at 1733 and 1714 cm^{-1}, ascribable to the C=O stretch of two types of the carboxylic species. This is evidence that the −CN groups underwent an incomplete hydrolysis to carboxylic groups during the synthesis. Spectrum b shows the presence of an intense band at ca. 1722 cm^{-1} due
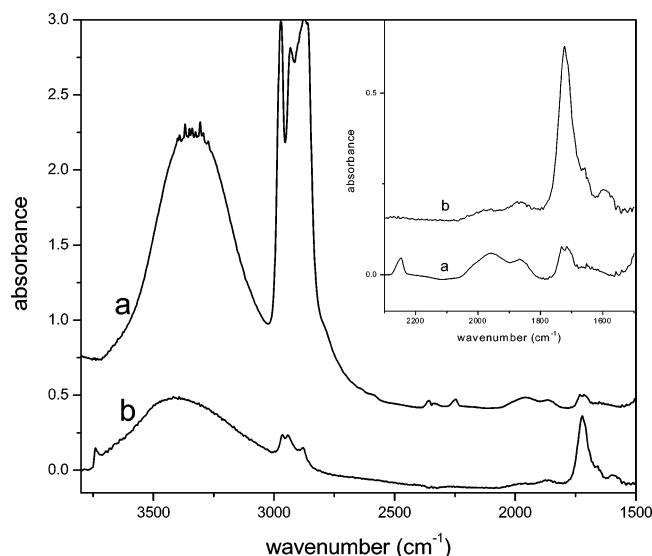
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Figure 3. Infrared spectra of the sample 7-COOH−SBA-15 after room-temperature outgassing. Curve a: as synthesized; curve b: after acid treatment. Inset: magnification of the 1500−2300 cm^{-1} region.
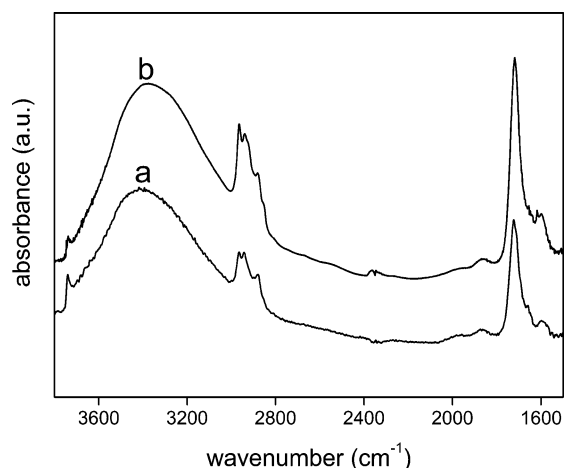

Figure 4. Infrared spectra of both samples after room-temperature outgassing: 7-COOH−SBA-15 (curve a) and 10-COOH−SBA-15 (curve b).

to the C=O stretching frequency, and no peak due to −CN groups, so showing that all −CN groups have been hydrolyzed.

Figure 4 shows the infrared spectra of 7-COOH−SBA-15 and 10-COOH−SBA-15 outgassed at room temperature. The C=O stretching band at 1722 cm^{-1} increases in intensity with COOH content, whereas negligible changes in frequency are observed. The weak band at 3736 cm^{-1} is due to quasi-isolated SiOH groups, whereas the broad band centered at ca. 3440 cm^{-1} is due to hydrogen-bonded silanols. Different interactions are possible, as SiOH species may interact with each other, as with plain silica, or with the carboxylic moieties at the surface, either at the oxygen atom in the C=O or the O−H groups. It is worth noting that the O−H stretch of the carboxylic group does not show up in the spectrum, though subsequent experiments definitely indicate their presence. Because of the nonrigid nature of the butyl arm, any carboxylic group is probably able to interact with an appropriate surface center with basic nature.

Figure 5a shows the infrared spectra of the 7-COOH−SBA-15 sample outgassed at 373, 473, 573, and 673 K. Thermal treatments cause dehydration of the surface, because silanols condense gradually to siloxane groups. The number of mutually interacting hydroxyl groups decreases, as shown by the decrease

of the band around 3440 cm^{-1}: the band due to isolated silanols becomes more intense and shifts to 3745 cm^{-1}, the value expected for truly isolated species. The −CH$_3$ mode at 2965 cm^{-1}, due to residual template, almost disappears between 573 and 673 K (a negligible shoulder is still visible at 673 K), whereas the −CH$_2$ bands only decrease, being related to the butyl chains of the functional groups. The carbonyl stretching band (Figure 5b) shifts from 1722 cm^{-1} (sample outgassed at 373 K) to 1752 cm^{-1} (sample outgassed at 673 K).

We ascribe such change in frequency to a change in polarity of the surface. The C=O species absorbing at lower frequency are those perturbed by the presence of silanols, whereas the C=O species absorbing at higher frequencies are "free" species. Indeed, the larger hypsochromic shift of the ν(C=O) band is observed between 373 and 473 K, because in this temperature range the sample dehydrates most; the smaller shift observed with further thermal treatments is probably related to a more limited decrease in silanol population. We also ascribe the limited changes in intensity of the C=O band due to a change in polarity of the surface: the overall population of C=O groups is probably constant, as TG experiments show that in the temperature range 373−673 K no weight loss, i.e., no release of CO$_2$ is observed. Note that a decrease in specific intensity is expected when the polarity of the medium is decreased.

The acidity of the system, as well as the accessibility of −COOH groups to reactants, was studied by dosing gaseous ammonia on the sample 7-COOH−SBA-15 outgassed at different temperatures and recording the infrared spectrum after each dosage. Figure 6a reports the IR spectra related to increasing equilibrium pressures of NH$_3$ on 7-COOH−SBA-15 outgassed at 473 K. The C=O stretching mode at 1722 cm^{-1} decreases and a two band appears at 1550 and 1407 cm^{-1}, due respectively to the asymmetric (ν_{as}) and symmetric (ν_s) stretching vibration of the carboxylate group COO$^-$. The band at 1722 cm^{-1} almost disappears, i.e., most COOH species react by ammonia. NH$_3$ strips the proton from COOH to give carboxylate anion COO$^-$ and ammonium ion (NH$_4^+$): a broad absorption corresponding to the NH$_4^+$ deformation vibration is observed at around 1456 cm^{-1}, more easily discernible in the difference spectra in Figure 6b. The signal at 1626 cm^{-1} observed at higher pressures is due to the bending mode of NH$_3$ gas.

Outgassing causes the disappearance of the bands due to ammonium and carboxylate species and the reappearance of the C=O peak, indicating that reaction is reversible:

$$-COOH + NH_3(g) \leftrightarrow -COO^- + NH_4^+ \qquad (1)$$
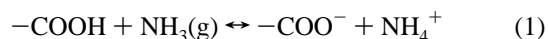
The occurrence of a reversible proton transfer to ammonia is noteworthy, because with acidic solids (e.g., zeolites) the reaction is irreversible, leading to NH$_4^+$ species stable up to 520 K. One reason for this behavior certainly is that carboxylic acids are intrinsically weak: a further reason is discussed below.

Adsorption of ammonia was also carried out on the sample outgassed at 573 and 673 K. Figure 7 compares the infrared spectra of the sample treated at 473, 573, and 673 K with the corresponding spectra recorded at the highest ammonia equilibrium pressure (100 mbar).

The proton-transfer reaction is observed, as indicated by the decrease of the C=O stretching mode and the appearance of carboxylate and ammonium peaks. The fraction of −COOH species interacting with ammonia at 100 Torr, however, decreases with pretreatment temperature, and is considerably lower for the sample treated at high temperature.
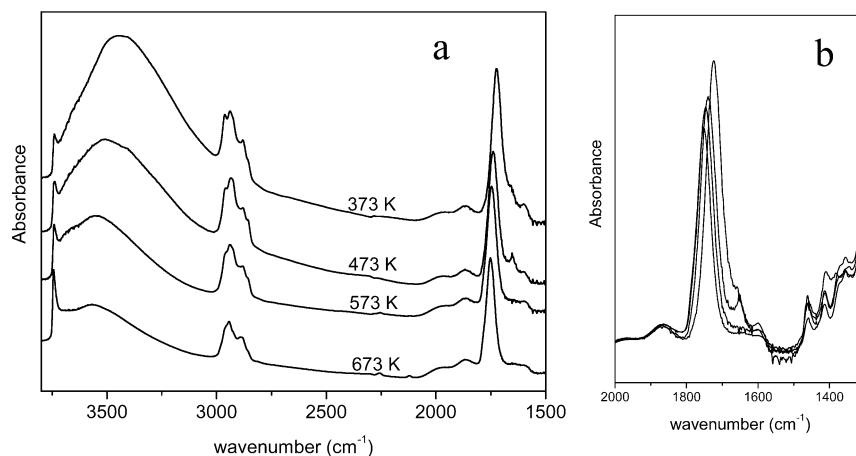
Figure 5. Infrared spectra of the sample 7-COOH−SBA-15 after thermal treatments. Section a: full spectra; section b: the C=O stretching mode region.
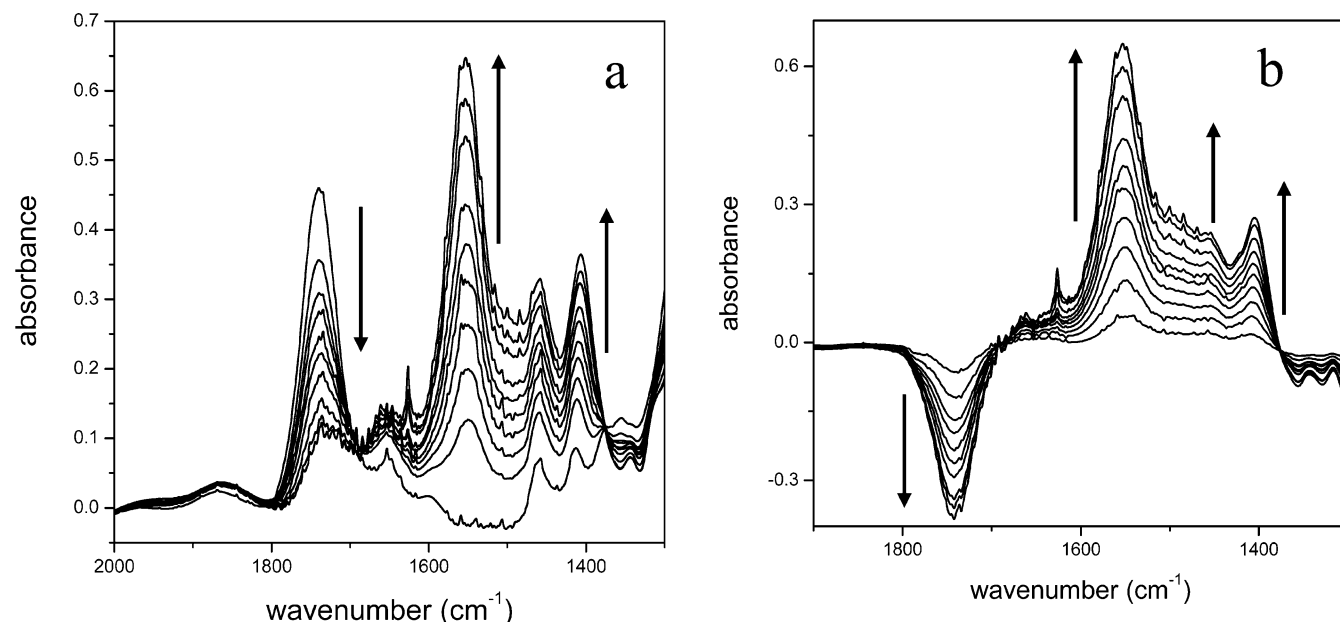

Figure 6. Infrared spectra concerning the interaction of ammonia with the sample 7-COOH−SBA-15. Section a: absorbance spectra; section b: difference spectra with respect to background. Ammonia equilibrium pressures in the range 0−100 mbar.
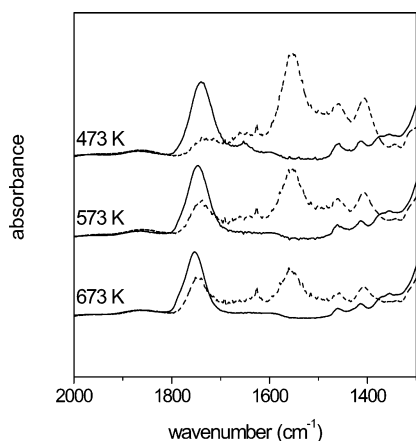

Figure 7. Comparison between the infrared spectra of the sample 7-COOH−SBA-15 outgassed at three different temperatures, before and after contact with 100 mbar NH$_3$ equilibrium pressure. Full curves: before contact; broken curves: after contact.

This may be either due to a decrease in the number of available −COOH groups or to a lower reactivity. To investigate whether irreversible structural rearrangements had occurred at

high temperature, e.g., causing the entrapment of the functional groups by rendering them inaccessible, the 7-COOH−SBA15 sample has been treated at 673 K, reexposed to air to allow its rehydration, and then outgassed again at 473 K. Ammonia dosage at ca. 100 mbar on this sample leads to IR spectra very similar to that observed for the sample merely treated at 473 K.

This result suggests that by increasing the outgassing temperature the carboxylic species do not become less accessible, but just less prone to reaction. To check this hypothesis, the behavior of the intensities of the carbonyl group at about 1720 cm^{-1} with ammonia equilibrium pressure was analyzed by assuming the same −COOH population in all three cases, and the corresponding equilibrium constants were calculated.

The equilibrium constant of the reaction is

$$K = [-COO^-][NH_4^+]/([-COOH]\, p_{NH_3}) \qquad (2)$$

The extent of reaction θ is the fraction of reacted carboxylic groups, also equal, because of stoichiometry to the fraction of carboxylate and ammonium species:

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$$\theta = [-COO^-] = [NH_4^+] \qquad (3)$$

The equilibrium constant may be written as

$$\theta^2/(1 - \theta) = K \, p_{NH_3} \qquad (4)$$

because $(1 - \theta)$ is the fraction of unreacted $-COOH$ groups, and p_{NH_3} the equilibrium ammonia pressure. θ can be calculated from the infrared spectra as $(I_{max} - I_i)/I_{max}$, where I_i = the intensity of the C=O peak at pressure p_i and I_{max} = the intensity of C=O peak in the absence of ammonia, slightly different from case to case.

By plotting $\theta^2/(1 - \theta)$ values as a function of p_{NH_3} for the samples outgassed at 473, 573, and 673 K, three straight lines passing through the origin were obtained (Figure 8), in agreement with equation reported above. The equilibrium constants resulted to be $K_{473K} = 2 \times 10^{-2}$ mbar^{-1}, $K_{573K} = 0.9 \times 10^{-2}$ mbar^{-1}, and $K_{673K} = 0.13 \times 10^{-2}$ mbar^{-1}, confirming a decrease of the COOH reactivity in the same order.

A probable reason for this result is the decrease in surface polarity upon increasing outgassing temperature, due to condensation of silanols with formation of nonpolar siloxane groups and isolated silanols, already invoked as the reason for the limited changes in frequency and specific absorption upon thermal treatment. These no longer provide a stabilizing polar environment for the proton-transfer reaction products, which is quite vital as observed for proton-transfer reactions in solutions, so leading to changes in the equilibrium constant of the process.

From a quantitative point of view, a fifteen-fold decrease in the equilibrium constant corresponds to an increase in $\Delta G°$, change in standard Gibbs free energy, of around 7 kJ. Considering that the standard entropy change $\Delta S°$ related to reaction 1 is likely to be the same irrespective of temperature of activation, one may ascribe the increase in $\Delta G°$ to a change in the interaction enthalpy, $\Delta H°$. The value obtained is indeed fully compatible with a van der Waals interaction with the surroundings.

Finally, the fact that the whole set of spectra can be interpreted assuming each time the highest intensity as I_{max} strongly suggest that all visible carboxylic groups may react with ammonia, i.e., all $-COOH$ species are available at the surface.

The low surface concentrations in $-COOH$ species of the two samples (ca. 0.9 and 0.45 COOH/nm^2, respectively) suggest that the carboxyl species are far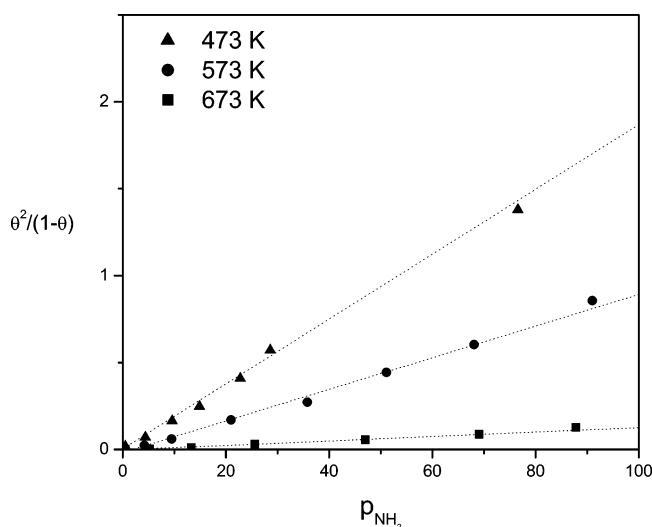 apart from each other, so they behave independently. This suggestion is supported by the observation that the intensity of C=O bands in Figure 4 is proportional to the experimentally established surface concentrations, and not, e.g., to the nominal concentrations in the batch. This conclusion validates the assumptions made in calculating equilibrium constants (eq 2). On the other hand, it allows the calculation of the molar extinction coefficient of the carbonyl band, which results 235 Km mol^{-1}.

Conclusions

IR spectroscopy shows that the carboxylic groups in an ordered SBA-15, incorporated via co-condensation, react reversibly at room temperature with ammonia, with the formation of carboxylate species $(-COO^-)$ and ammonium ions (NH$_4^+$). The apparent reluctance to reaction of carboxylic groups on samples outgassed at relatively high temperatures is ascribed to a destabilization of the reaction products (the ionic carboxylate/ ammonium pair) brought about by the decrease in polarity of the silica surface. This phenomenon finds correspondence with the features of proton-transfer processes in solution.

The reversible nature of the proton transfer allows the calculation of the related equilibrium constant, which is found indeed to decrease with increasing outgassing temperature, so confirming a decrease in the $-COOH$ reactivity. The corresponding decrease in Gibbs free energy is compatible with the loss of a van der Waals interaction (e.g., H-bonding) stabilizing the reaction products.

All carboxylic species seem to be available for reaction at any studied pretreatment temperature and therefore seem to be isolated and non interacting with each other.

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Figure 8. Plot of $\theta^2/(1 - \theta)$ as a function of NH$_3$ equilibrium pressure for the sample 7-COOH−SBA-15 outgassed at 473 K, 573 K, 673 K.