Formaldehyde oligomerization on silicalite: an FTIR and NMR study

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Upon adsorption of formaldehyde onto silicalite, hydrogen-bonded adducts are formed between the (slightly acidic) SiOH groups of the purely siliceous zeolite and formaldehyde, as seen by using both FTIR and ^{1}H-NMR spectroscopies. These species then evolve to form polymerization products of the type $-(CH_2O)_n-$. On the contrary, when silicalite is contacted with trioxane hydrogen-bonded adducts are formed, but no polymerization ensues.

KEY WORDS: formaldehyde polymerization; FTIR spectroscopy; ^{1}H-NMR spectroscopy; silicalite; zeolites.

1. Introduction

Zeolites and related porous solids can be used as size-selective polymerization catalysts. Both, acid and redox based catalytic processes have been reported [1–4] in this context. Besides applications in the wider chemical industry, polymerization of monomer species inside the channels of zeolites can lead to nano-composite materials having organic polymer chains embedded in the inorganic zeolite matrix. Such composite materials offer potential applications in a number of fields, including molecular electronics and chemical sensing [5].

In the course of a study on formaldehyde polymerization on acidic zeolites, we investigated (as a reference system) oligomerization on silicalite-1, a purely siliceous zeolite having the MFI structure type [6]. By means of FTIR and MAS NMR spectroscopy, it was found that oligomerization readily takes place when paraformaldehyde is used as a formaldehyde precursor. However, trioxane (the cyclic trimer of formaldehyde) does not give rise to any polymerization process.

2. Experimental

The silicalite-1 sample used was synthesized following standard procedures [7]. Powder X-ray diffraction showed good crystallinity and confirmed the expected MFI structure type [6]. For FTIR measurements, the sample (in the form of a thin self-supported wafer) was activated (outgassed) at 723 K for 2 h under a vacuum before use. The IR spectra were recorded with a Bruker IFS66 instrument at a resolution of 2 cm^{-1}. For NMR measurements, the sample was packed inside a zirconia rotor (diameter 4 mm) and activated under a vacuum at 623 K for 12 h, followed by two additional hours at 723 K. The whole process was carried out inside a home-made cell that allowed thermal treatments, gas dosage and transfer to the NMR measurement chamber to be done under a controlled atmosphere. This was necessary to avoid undesired contamination of the sample by atmospheric water. The solid state MAS ^{1}H-NMR spectra were recorded with a Bruker MSL 200 instrument, working at 200.132 MHz and at a spinning rate of 10^4 rpm.

Pure formaldehyde is not commercially available. It is usually supplied as a ca. 37% CH_2O solution in water, to which methanol (or another stabiliser) is added to avoid polymerization. For this reason, precursors of (monomeric) formaldehyde are commonly used for spectroscopic studies. As a formaldehyde precursor, paraformaldehyde (a polymer of formaldehyde with a low molecular weight) was used. To this end, paraformaldehyde (Aldrich, 95%) was thermally decomposed at 373 K under a vacuum, and the formaldehyde thus obtained was collected in a gas reservoir and then dosed onto the silicalite sample. In order to avoid the undesired presence of water vapor at this stage, a trap containing anhydrous Na_2SO_4 was placed between the reservoir containing paraformaldehyde and the balloon where formaldehyde was collected. As an alternative to paraformaldehyde, 1,3,5-trioxane (the cyclic trimer of formaldehyde) was also investigated.

3. Results and discussion

3.1. FTIR characterization

Increasing doses of formaldehyde (up to an equilibrium pressure of about 5.5 mbar) were contacted at

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room temperature with the silicalite-1 sample. The FTIR spectra recorded after each dose are presented in figure 1, in the 3800–2250 and 1800–1300 cm^{-1} spectral regions (parts a and b, respectively). The spectra in part b have been background subtracted.

The spectrum of the silicalite sample (dotted line in part a) shows two bands, at 3742 and at 3495 cm^{-1}. These bands correspond, respectively, to the O–H stretching modes of free (isolated) silanols and to silanol groups perturbed by mutual hydrogen bond interactions (hydroxyl nests) [8,9]. At the lowest doses of formaldehyde the predominant species are hydrogen-bonded adducts formed between formaldehyde (through the oxygen lone pair) and the SiOH groups of silicalite. This is shown by: (i) the progressive erosion of the band at 3742 cm^{-1} as the equilibrium pressure of formaldehyde increases; the attendant appearance of a new, broad band at about 3445 cm^{-1} (i.e., ~300 cm^{-1} red shifted); and the formation of an isosbestic point at 3661 cm^{-1} (figure 1a); and (ii) a red-shift of the ν(C=O) stretching mode of formaldehdye, from 1746 (in free formaldehyde [10,11]) to 1726 cm^{-1} (figure 1b). The bending mode of formaldehyde, $\delta(CH_2)$, in the hydrogen-bonded adduct appears at 1500 cm^{-1}, nearly unperturbed with respect to the corresponding value for gas-phase formaldehyde. This result indicates that the ν(C=O) and $\delta(CH_2)$ modes are coupled in hydrogen-bonded formaldehyde, so that the expected blue shift of the $\delta(CH_2)$ when formaldehyde interacts via hydrogen bonding is partially compensated by the induced red shift of the ν(C=O) mode. Finally, the absorption bands due to the symmetric and asymmetric C–H stretching modes of hydrogen bonded formaldehyde appear (with a very low intensity) at 2833 and 2894 cm^{-1}, respectively; i.e., about 50 cm^{-1} blue shifted with respect to the free molecule (see inset in figure 1a). These spectroscopic features are completely analogous to those previously observed for formaldehyde interacting with both silica and alumina [12]. A detailed inspection of the ν(C=O) mode reveals the complex nature of this band, which presents a component at 1716 cm^{-1} that predominates at the lowest equilibrium pressure (figure 1b). This component can also be assigned to hydrogen-bonded adducts of formaldehyde with acid sites slightly stronger than those giving rise to the main IR absorption band at 1726 cm^{-1} (possibly involving the hydroxyl nests of the material).

As the equilibrium pressure of formaldehyde increases, the formation of additional bands is clearly observed in both, the C–H stretching region and below 1500 cm^{-1}. In particular, two relatively intense bands appear at 2982 and 2918 cm^{-1}, as well as a weaker component at 2810–2800 cm^{-1} (figure 1a). In the low frequency region of the spectra, main bands are observed at 1474, 1436 and 1407 cm^{-1}; all of them having a composite nature (figure 1b). The similarities of all these features with the spectrum of polyoxomethylene (the homopolymer of formaldehyde [13]) indicates that polymerization of formaldehyde readily takes place

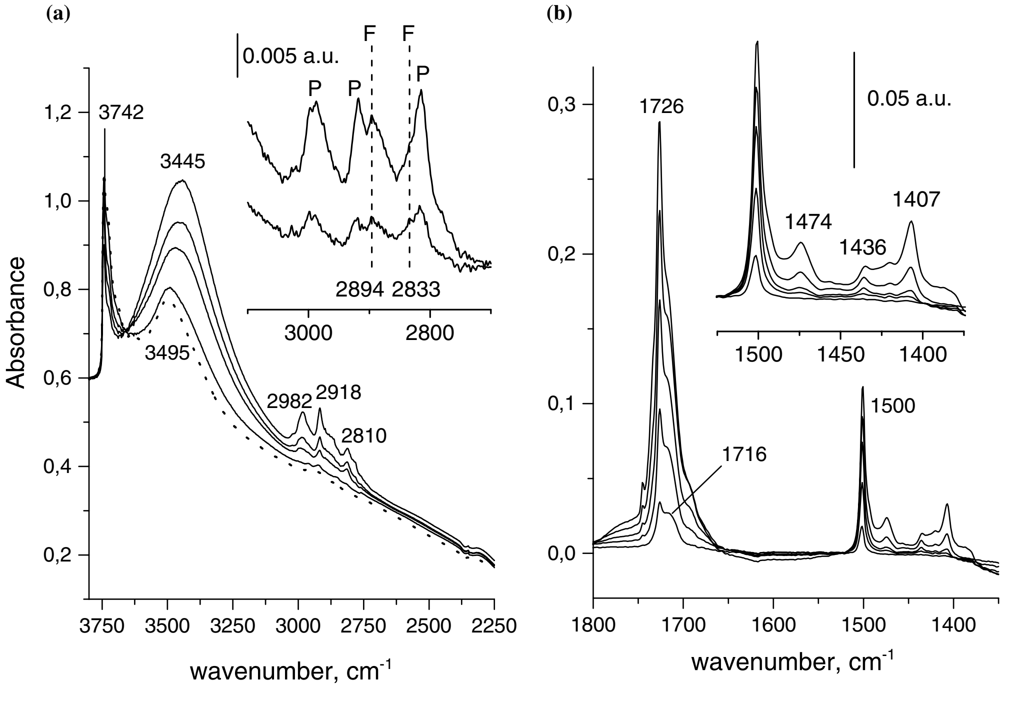

Figure 1. (a) FTIR spectra, in the 3800–2250 cm^{-1} spectral region, of increasing doses of formaldehyde adsorbed onto silicalite. The inset shows an enlarged view of the ν(C–H) region at the lowest doses of formaldehyde, where the absorption bands corresponding to hydrogen-bonded formaldehyde are observed. F stands for hydrogen-bonded formaldehyde and P for polyoxomethylene. (b) Same spectra as in part a, in the 1800–1350 cm^{-1} spectral region. The inset shows a detail of the 1500–1350 cm^{-1} region.

when the monomer is adsorbed on silicalite. This result shows that the silanol groups of the material are strong enough to catalyze the polymerization of monomeric formaldehyde units (as obtained from thermally decomposed paraformaldehyde). It should be noted that the gas phase IR spectrum of thermally decomposed paraformaldehyde showed no traces of polymeric species. It is also worth mentioning that a fraction of the dosed formaldehyde remains as a physisorbed monomer (IR absorption band at 1745 cm^{-1}, figure 1b).

The IR spectra in figure 1 do not show any evidence for the formation of cyclic oligomers (such as trioxane), which would bring about the corresponding spectroscopic features, distinct form those of linear oligomeric species (*vide infra*). Hence, it is inferred that in the experimental conditions used, only linear formaldehyde oligomers are formed.

A different situation was found for trioxane. In contrast with the results commented above, the FTIR spectra obtained after interaction of trioxane with silicalite, shown in figure 2, do not reveal formation of polymerization products. The bands observed in the ν(C–H) and in the 1550–1400 cm^{-1} spectral regions correspond to those of pure trioxane [14], although slightly perturbed by the formation of hydrogen bonds with the silanol groups of the material. The formation of such hydrogen bonds is also revealed by erosion of the band at 3742 cm^{-1} as the equilibrium pressure of trioxane increases, and by the development of a broad and intense band at ca. 3400 cm^{-1}.

This result was not unexpected, on account of the fact that before polymerization starts it is necessary to produce (assisted) ring opening of trioxane; a process that is known to occur when mineral acids or Friedel–Crafts catalysts are used. However, according to the present results, it is clear that the silanol groups of silicalite are not acidic enough to bring about ring opening of trioxane.

3.2. ^{1}H-NMR characterization

Figure 3a shows the ^{1}H-NMR spectra obtained after contacting the silicalite sample with increasing doses of CD_2O. Deuterated formaldehyde was obtained by decomposing deuterated paraformaldehyde (Aldrich, 99 at% D), following the same procedure as described in Section 3.1 for paraformaldehyde.

The ^{1}H-NMR spectrum of the blank silicalite sample (dotted line in figure 3a) presents a narrow band at 1.9 ppm, together with a broad tail extending up to 6 ppm. Following the existing literature on the field [15–19], the former band is assigned to the ^{1}H signal of the hydrogen atoms of free silanols, while the latter corresponds to SiOH groups perturbed by hydrogen bonding interactions. However, it should be borne in mind that any small amount of adsorbed water, which

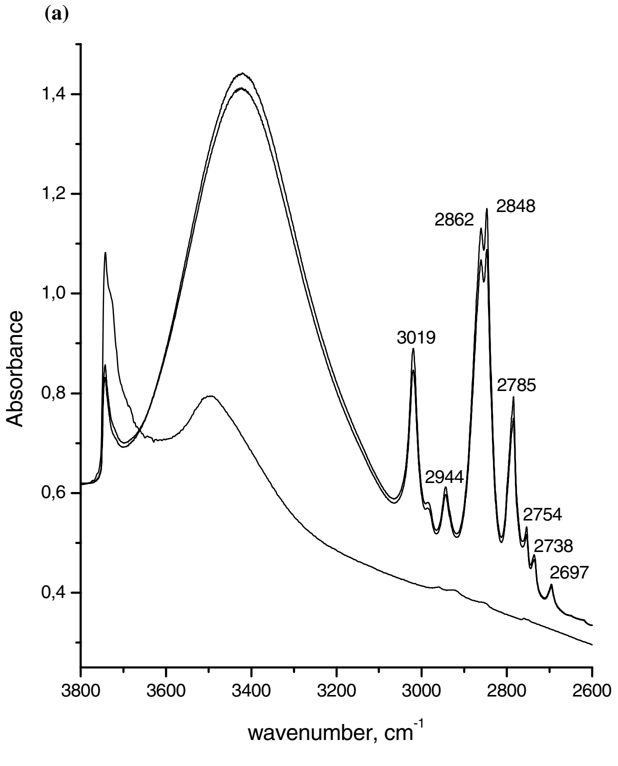

Figure 2. FTIR spectra of increasing doses of trioxane adsorbed onto silicalite, in the 3800–2600 and 1550–1350 cm^{-1} regions, in parts a and b, respectively.

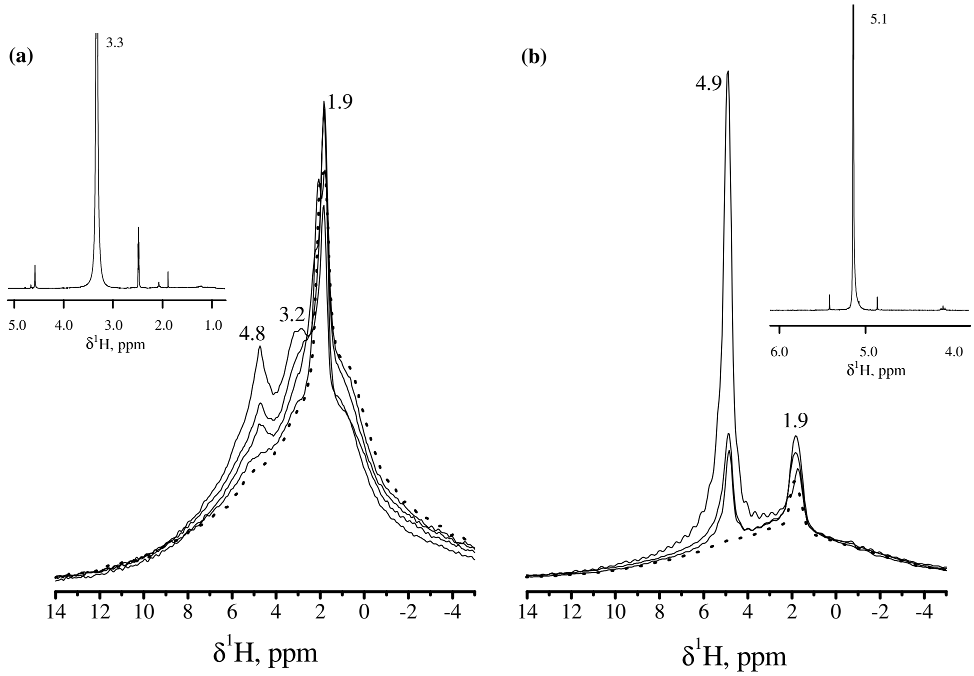

Figure 3. (a) ^{1}H-NMR spectra of deuterated formaldehyde adsorbed onto silicalite. The inset shows the ^{1}H-NMR spectrum of pure paraformaldehyde in dimethylsulfoxide solution. (b) ^{1}H-NMR spectrum of trioxane adsorbed onto silicalite. The inset shows the ^{1}H-NMR spectrum of pure trioxane in CD_2Cl_2 solution.

could be present in the sample, would also contribute to the broad tail of the ^{1}H-NMR line.

After the interaction of silicalite with formaldehyde, a progressive erosion of the band at 1.9 ppm is observed, which is accompanied by the concomitant development of a new signal at 4.8 ppm. These results indicate that upon adsorption of formaldehyde, hydrogen-bonded adducts between silanols and formaldehyde are formed. As a consequence of this process, the ^{1}H signal of silanols is shifted up to 4.8 ppm ($\Delta\delta(^1H) = 2.9$ ppm). Similar values of $\Delta\delta(^1H)$ have been observed for silanols in interaction with molecules of comparable basic strength, such as acetonitrile ($\Delta\delta(^1H) = 3.2$ ppm [20]).

Upon increasing the equilibrium pressure of formaldehyde, an additional signal at 3.2 ppm gradually develops. This signal is assigned to the formation of oligomeric species of the type $–(CH_2O)_n–$. Although deuterated formaldehyde was used in the NMR measurements, isotopic exchange between deuterium of CD_2O and protons of silicalite (and also possibly traces of adsorbed water) can occur. This fact would explain the presence of the NMR signal at 3.2 ppm. In favor of the above assignment, it can be added that the ^{1}H-NMR spectrum of paraformaldehyde in dimethyl sulfoxide solution shows a singlet at 3.3 ppm (see inset in figure 3a).

In conclusion, the NMR measurements confirm that polymerization of formaldehyde takes place upon interaction of the monomer with the silanol groups of silicalite, in agreement with the results obtained from FTIR spectroscopy.

Finally, the ^{1}H-NMR spectra obtained after the adsorption of trioxane onto silicalite are shown in figure 3b. Note that in this case $C_3H_6O_3$ (non-deuterated trioxane) was used, so that the signal coming from hydrogen atoms of trioxane also contributes to the final ^{1}H-NMR spectra.

As the equilibrium pressure of trioxane increases, a narrow peak at 4.9 ppm gradually appears, and it dominates the spectrum at the highest doses of trioxane. The intensity of this signal is too large to be attributed to SiOH groups of silicalite. Therefore, the peak at 4.9 ppm is assigned to the hydrogen atoms of trioxane, possibly in hydrogen-bonding interaction with silanol groups of silicalite (as was inferred from the corresponding FTIR spectra shown in figure 2a). Note that, the ^{1}H-NMR spectrum of trioxane in CD_2Cl_2 solution (inset in figure 3b) shows a singlet at 5.1 ppm, which lends support to the above assignment. Again, no polymerization products were detected by NMR spectroscopy when trioxane was contacted with silicalite, thus confirming that silicalite does not have enough acidity to cause ring opening of trioxane.

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