Morpholine, an in Situ ^{13}C NMR pH Meter for Hydrothermal Crystallogenesis of SAPO-34

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The pH has been measured in situ by ^{13}C NMR during hydrothermal formation of SAPO-34 (SAPO: silicoaluminophosphate) in the presence of hydrofluoric acid and with morpholine as the structure-directing agent. Morpholine, with a pK_a of about 8.8 at room temperature, can be used as a pH probe within the region $7.3 < \mathrm{pH} < 10.3$. The pH was determined to be 5.5 immediately after mixing of the gel and increased by 3 pH units during the synthesis. During the first stage of the heating (25−85 °C), no change in pH was observed by using a conventional pH meter. During formation of the layered intermediate prephase (85−120 °C), the pH increased by ~2 units. A second sharp pH increase was observed by in situ ^{13}C NMR when the synthesis temperature approached 160−165 °C, which corresponded to the minimum temperature needed to prepare triclinic SAPO-34 within a reasonable time frame (a few days).

Introduction

The demand for new functional materials is steadily increasing and rational design of novel materials with desired properties are of vital interest for further technological development. Of particular interest to catalysis, adsorption, and separation technology are the microporous materials such as $AlPO_4$s and SAPOs (silicoaluminophosphates). They are usually prepared by nucleation and subsequent crystal growth in complex gel systems under hydrothermal conditions. When the mechanism of condensation, nucleation, and crystallization of such nanomaterials is being established, the pH evolution is critical information to collect.

In situ pH measurements as a function of synthesis time and temperature would provide valuable insight into the physiochemical processes in the gel system during hydrothermal crystallization. One of the most significant achievements in high-temperature potentiometry was the development of the yttria-stabilized zirconia membrane sensors, applied in potentiometric measurements of high subcritical and supercritical systems up to 450 °C.[1,2] Also, potentiometric (silver−silver chloride,[3] platinum−hydrogen,[4] and gold−hydrogen[5]) electrodes are developed for temperatures and pressures up to approximately 400 °C and 34 MPa, respectively. However, these pH sensors are not viable toward corrosive media, such as the fluoride ions that are present in the gel system under study.

The use of in situ techniques have become well-established for following hydrothermal crystallizations.[6,7] In the present study, high-resolution ^{13}C NMR has been used for in situ pH measurements during the formation of SAPO-34 in the presence of HF, making use of morpholine, the structure-directing agent, as the pH probe.

Background and Calibration of the pH Measurements. In a former ex situ study, Hansen and coworkers[8,9] demonstrated that the ^{1}H and ^{13}C NMR chemical shift of morpholine appears not to be sensitive to changes in the reaction medium. Thus, morpholine can be used as the pH probe of the SAPO gel. Usually, the pH evolution has been surveyed by ex situ measurements (quenching); however, Gerardin et al.[10] recently provided a comprehensive coverage of NMR pH-metry methodology at high temperature using the ^{14}N NMR chemical shifts of imidazole and DABCO (1,4-diazabicyclo[2.2.2]octane). Fast chemical exchange, compared with the NMR time scale, results in an averaged chemical shift of the nuclei in the protonated (mH$^+$) and the nonprotonated (m) morpholine states. Thus, the observed chemical shift represents the arithmetic

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mean distribution of the protonated and nonprotonated morpholine and the degree of protonation can be calculated:

$$\delta_{\mathrm{obs}} = \frac{[m]}{[m] + [m\mathrm{H}^+]}\delta_{\mathrm{B}} + \frac{[m\mathrm{H}^+]}{[m] + [m\mathrm{H}^+]}\delta_{\mathrm{BH}^+} \qquad (1)$$

By introduction of the dissociation constant of morpholine,

$$k_{\mathrm{a}} = \frac{[m][\mathrm{H}^+]}{[m\mathrm{H}^+]} \qquad (2)$$

The observed chemical shift can easily be expressed as a function of pH,

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{\delta_{\mathrm{obs}} - \delta_{m\mathrm{H}^+}}{\delta_m - \delta_{\mathrm{obs}}} \qquad (3)$$

where δ_{obs} represents the observed chemical shift, $\delta_{m\mathrm{H}^+}$ and δ_m represent the chemical shift of strong acidic and strong alkaline morpholine reference solutions, respectively, and $\mathrm{pK_a}$ is the dissociation constant of morpholine. The three latter parameters are temperature-dependent and calibration measurements are necessary.

Experimental Section

Chemicals and Mixing Procedures. Calibrations of the ^{13}C NMR chemical shifts of $m\mathrm{H}^+$ and m as a function of temperature were performed on morpholine–water solutions. The pH was adjusted by adding either 6 M HNO_3 or NaOH(s). The final morpholine–water molar ratios were 2.1:60, corresponding to a morpholine concentration of 1.66 M.

Synthesis gels of chemical composition 2.1:1.0:1.0:1.0:1.0:60 morpholine:SiO_2:Al_2O_3:P_2O_5:HF:H_2O (molar ratio)[9] were prepared by first mixing one-fourth of the deionized water with phosphoric acid (85 wt %, Merck) together with the aluminum source (Catapal-B, Vista Chemicals). The mixture, labeled solution A, was then stirred well before further addition of one-fourth of deionized water. Solution B was prepared by mixing Ludox LS-30 (Du Pont), morpholine (Acros Organics)m and another one-fourth of the water. This solution was then slowly added to solution A during intense mixing, before the last one-fourth of the water was added. Subsequently, 1 equiv of 40 wt % HF (Fluka) was added at the end of the preparation. The synthesis time and temperature in ordinary 50-mL Teflon-lined steel autoclaves was 4–6 h and 200 °C.

Characterization

NMR. Hydrothermal in situ ^{13}C and ^{14}N high-resolution NMR spectra were recorded on an MSL300 Bruker spectrometer at temperatures up to 170 °C. The syntheses were carried out in a specially made high-pressure Vespel tube protected with a Teflon insert (10-mm o.d., 8-mm i.d.).[11,12] The tube can withstand temperatures up to 250 °C and a pressure of ~50 bar. The Teflon liner protects the Vespel tube from the reagents, including HF and the morpholine. All the tube materials exhibit diamagnetic properties and are transparent to r.f. waves. A Bruker VT3000 variable-temperature unit was used to regulate the heating airflow. The actual internal temperature of the sample was calibrated using the ethylene glycol proton NMR method,[13] and the heating profile was measured by introducing a Copper–Constantan thermocouple (type T) into an open hydrothermal tube filled with Kryotox oil during a heating/cooling sequence. The ^{13}C chemical shifts were referenced to TMS as an external standard.

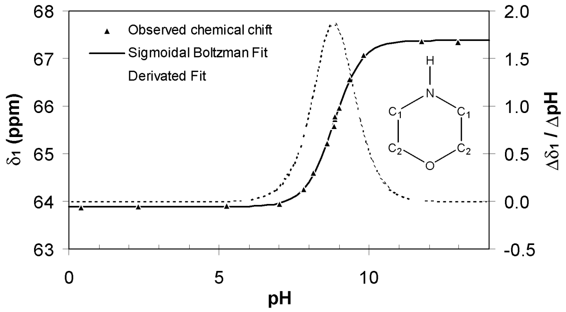

Figure 1. ^{13}C NMR titration curve and indication of the pH-sensitivity region of morpholine at room temperature (results from the C_1 carbon positions).

Table 1. ^{13}C NMR Characteristics of Morpholine as a pH Probe at Room Temperature

peak	$\Delta\delta$ (ppm)	$\Delta\delta/\Delta$pH	$\mathrm{pK_a}$	pH probe range[a]
δ_1	3.49 ± 0.02	1.88	8.81 ± 0.01	7.3–10.3
δ_2	1.40 ± 0.02	0.75	8.88 ± 0.02	7.4–10.4
$\delta_1 - \delta_2$	2.08 ± 0.02	1.14	8.77 ± 0.01	7.3–10.2

[a] Determined as the region where $\delta\Delta/\mathrm{pH} > 15\%$ of $(\delta\Delta/\mathrm{pH})_{\max}$.

Ex Situ pH Measurements. They were performed with an Orion 420A pH meter equipped with a pH Orion triode electrode with an Ag/AgCl internal reference.

XRD. Powder X-ray diffraction patterns of the final synthesis products obtained from the NMR tube and conventional steel autoclave syntheses were compared to ensure that the synthesis conditions in the NMR experiments were comparable to the autoclave syntheses. XRD patterns were collected on a Siemens D5000 diffractometer. The instrument was equipped with a Ge fully focusing primary monochromator (Cu Kα_1 radiation, $\lambda = 1.540560$ Å) and a Brown 16° position sensitive flat PSD detector. The step size used was 0.0160° (step time 1.0 s) and the scan range was 3–40° (2θ).

Results

pH Calibration. Morpholine contains two distinct carbon positions, C_1 and C_2 (see structure insert in Figure 1), the chemical shift of which are both pH-sensitive. As their pH dependency is not the same, the difference in the two chemical shifts ($\delta_{C1} - \delta_{C2}$) is also pH-dependent. Morpholine–water solutions were examined as a function of pH to determine the morpholine sensitivity as a pH probe. The observed and fitted "NMR titration curve" obtained from the C_1 carbon atoms at room temperature are displayed in Figure 1. The maximum pH sensitivity was determined as 1.88 ppm/pH unit from the derived sigmoidal Boltzman fit. It was shown earlier that other interactions than pH between morpholine and the components of the reaction, present in the gel, do not significantly influence the chemical shift.[9] It is thus obvious, from Figure 1, that morpholine can be used as a sensitive pH probe within the region $7.3 < \mathrm{pH} < 10.3$. The characteristics of the different ^{13}C NMR signals are summarized in Table 1.

The ^{13}C NMR chemical shifts of strong acidic and strong alkaline morpholine–water solutions were recorded as a function of temperature in the hydrothermal tube (parts a and b, respectively, in Figure 2). Linear interpolations were carried out and the temperature

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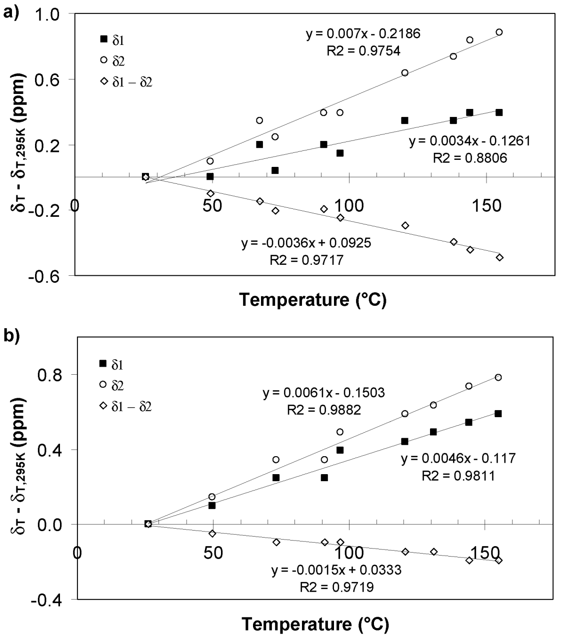

Figure 2. ^{13}C NMR chemical shift as a function of temperature within (a) strong acidic and (b) strong alkaline morpholine solution.

dependence of the ^{13}C NMR chemical shifts can be expressed as

$$\delta_{1,m} = 0.0046 \times T + 66.01 \qquad R^2 = 0.981$$

$$\delta_{1,m\mathrm{H}^+} = 0.0036 \times T + 62.81 \qquad R^2 = 0.927$$

$$\delta_{2,m} = 0.0061 \times T + 43.23 \qquad R^2 = 0.988$$

$$\delta_{2,m\mathrm{H}^+} = 0.0070 \times T + 41.53 \qquad R^2 = 0.975$$

$$\delta_1 - \delta_{2,m} = -0.0015 \times T + 22.79 \qquad R^2 = 0.972$$

$$\delta_1 - \delta_{2,m\mathrm{H}^+} = -0.0036 \times T + 21.36 \qquad R^2 = 0.972$$

The dissociation constant of morpholine as a function of temperature was determined by potentiometric pH measurement of a morpholine−water solution (2.1:60 ratio) while varying the temperature within the range 0−50 °C. The mixture was initially adjusted to pH = 8.78, corresponding to the middle of the buffer region (Figure 1). The pH was plotted as a function of 1/*T* and pK$_a$ values at higher temperatures were obtained by linear extrapolation (Figure 3a). The determined temperature dependence of pK$_a$ can be expressed as

$$\mathrm{pK_a} = 1.56 \times 10^3 \times 1/T + 3.52 \qquad R^2 = 0.996$$

and is displayed in Figure 3b together with the neutral pH condition as a function of temperature.

Ex Situ pH Measurements. pH measurements of the synthesis gel prior to heating and after the hydrothermal treatment at 180 °C in a 50-mL Teflon-lined steel autoclave indicated an increase from ~5.5 to ~8.6 during the synthesis. The initial gel pH was outside the detection window of the morpholine pH probe. The addition of other amines, like imidazole (pK$_a$ = 7) or DABCO (pK$_a$ = 3 and 8.9) could extend the pH window; however, by using morpholine, the system was not chemically perturbed.

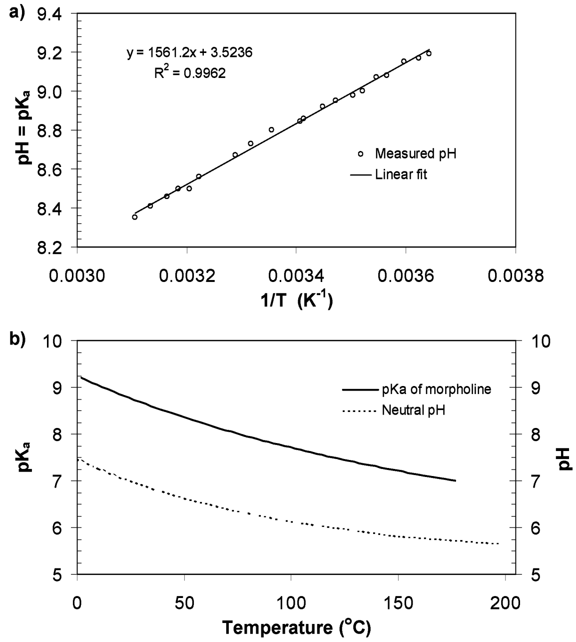

Figure 3. (a) pH of a morpholine−water solution as a function of 1/*T* and (b) the pK$_a$ values obtained from extrapolation. The pH corresponding to neutral conditions as a function of temperature is included as well.

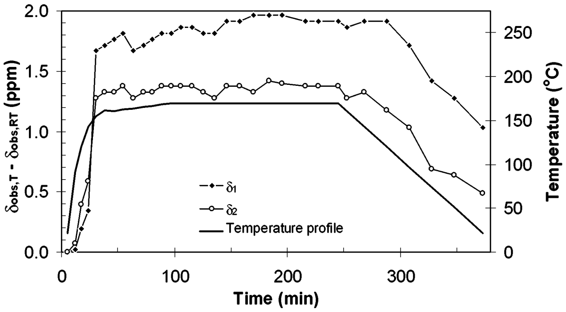

Figure 4. In situ ^{13}C NMR chemical shift variations as a function of temperature and time.

Due to the lack of sensitivity of the morpholine pH probe within the pH range 5.5−7.3, potentiometric pH measurements were performed on a gel when heating from room temperature to 85 °C in an oil bath. Only pH variations according to the increased dissociation of water as a function of temperature were observed.

In Situ NMR pH Measurements. The observed ^{13}C NMR chemical shifts recorded during the synthesis as a function of temperature and time are shown in Figure 4. Due to its higher sensitivity, the chemical shift of the C$_1$-peak was used to calculate the pH evolution according to eq 3, taking account of the temperature dependency of δ_m and $\delta_{m\mathrm{H}^+}$. Figure 5 displays the pH inside the hydrothermal tube adjusted to 25 °C. By introduction of the temperature dependency of pK$_a$ of morpholine and of pK$_w$ of water in eq 3, the pH at higher temperatures can be calculated (Figure 5). The temperature profile and conditions representing neutral pH are included in the figure as well. The linear pH increase during the period of cooling can be directly correlated to the decreased dissociation of water as a function of temperature.

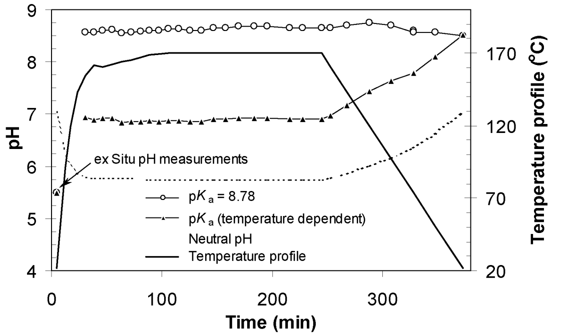

Figure 5. Calculated pH evolution throughout synthesis of SAPO-34. Heating profile and neutral pH conditions are included as well.

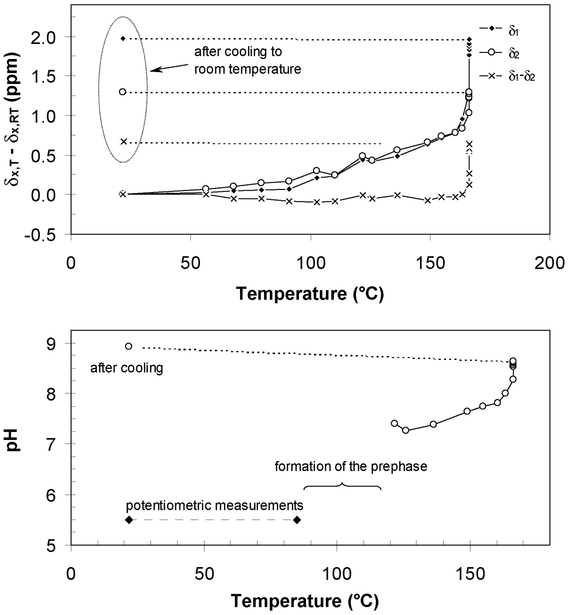

Figure 6. In situ ^{13}C NMR synthesis with stepwise heating: (a) the chemical shift variations (the last point was recorded after cooling to room temperature) and (b) the calculated pH profile.

The pH increased from ~5.5 to ~8.6 during the heating stage and remained essentially constant throughout the crystallization and the cooling period. To gain an improved insight into the pH evolution during the heating stage, an in situ NMR synthesis with stepwise heating was performed. The variation of the ^{13}C NMR chemical shift as a function of temperature/time and the calculated pH evolution are shown in parts a and b, respectively, of Figure 6. The morpholine pH probe became sensitive when the temperature reached 120 °C and the pH was calculated as 7.3. A slight pH increase was observed by further heating before a sharp increase to pH = 8.6 when the temperature reached 160 °C. When the potentiometric measurements up to 85 °C were included, it appears that the pH remained constant during the first part of the heating program. Within the temperature range 85−120 °C, the pH increased from 5.5 to 7.3. Furthermore, a minimum temperature of ~160−165 °C was needed to activate the second pH increase.

Initial attempts were performed to make use of the ^{14}N NMR chemical shift to measure the pH. The sensitivity ($\Delta\delta/\Delta$pH) was expected to be higher because of the direct influence of the protonation on the nitrogen atom compared to the more remote carbons.[10] However, the signal disappeared when high temperatures were reached and it reappeared during the cooling stage. It was therefore not possible to establish any relations between these observations and the formation of the layered $AlPO_4F$ precursor phase formed at intermediate temperature.[14,15] This indicates a dynamic exchange process activated by the temperature increase, which results in significant broadening and extinction of the signal. The broadening of the ^{14}N NMR morpholine signal (low $\Delta\delta$/fwhm value) resulted in insufficient sensitivity, even at intermediate temperature.

Discussion

Generally, when $AlPO_4$ and SAPO materials are being formed, a sharp increase of 2−3 pH units during the first few hours of synthesis are observed before the pH stabilizes. The pH variations are not reversible throughout a heating/cooling cycle. Prior to heating, the pH was in the weak acidic region and the gel system contained hexacoordinated aluminophosphate and fluoroaluminophosphate complexes and an amorphous solid $Al(OH,F,H_xPO_4)_3$ phase, among others.[9] During the heating stage, the critical prephase, which is crucial for the formation of SAPO-34,[14] formed around 90−95 °C. It transforms to SAPO-34 when it is heated to ~165−185 °C through a solution-mediated mechanism.

During the first stage of heating (T < 85 °C), no significant pH variations were detected (potentiometric measurements). When morpholine was used as the pH probe, the pH increase from 5.5 to 7.3 could not be monitored. However, from the stepwise heating experiment, a pH of 7.3 was measured when the temperature reached 120 °C. A significant decrease of phosphorus, aluminum, and fluorine in the solution was observed by in situ NMR when the prephase was being formed.[15] It is reasonable to assume a pH increase related to the consumption of phosphates. At T > 120 °C, in situ ^{13}C NMR was used to follow the pH evolution throughout the rest of the synthesis. When the temperature approached 160−165 °C, a sharp pH increase to ~8.6 was measured. This temperature roughly corresponds to the minimum synthesis temperature needed to produce the triclinic SAPO-34 phase in conventional steel autoclaves (within a reasonable time frame, a few days).[14] Moreover, simultaneously with the abrupt pH increase, a high degree of supersaturation of aluminum in the solution was detected.[15] It seems reasonable to assume that nucleation of the SAPO-34 phase was activated by a high degree of supersaturation, generated by redissolution of the prephase as a result of the pH and the temperature increase.

It follows from the results that morpholine is a good pH probe for the pH range of 7.3−10.3, a range a little limited for the system under investigation. However, in combination with potentiometric measurements, the main features of the pH evolution are monitored. Alternatively, by addition of other amines such as imidazole, which might be used as a sensitive pH probe in the range ~4.0−7.0,[10] the complete pH evolution

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could be monitored by in situ NMR. However, addition of other amines influences the crystallization mechanism, kinetics, pH, and so forth. For instance, when the gel ratio used in this study is kept, it has been shown that imidazole can be used as a structure-directing agent for the formation of SAPO-34, interfering therefore with the crystallization.[16]

Conclusion

It has been demonstrated that morpholine can be used as a pH probe in a pH range of 3 units (7.3−10.3). The pH increased in a two-step manner during synthesis of SAPO-34. The first step took place during the formation of the intermediate prephase. In a parallel study,[15] a large decrease of phosphate concentration in solution was simultaneously observed. A second sharp pH increase was observed when the final synthesis temperature was being approached, which is ascribed to the redissolution of the intermediate prephase when the SAPO-34 phase is being recrystallized.

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