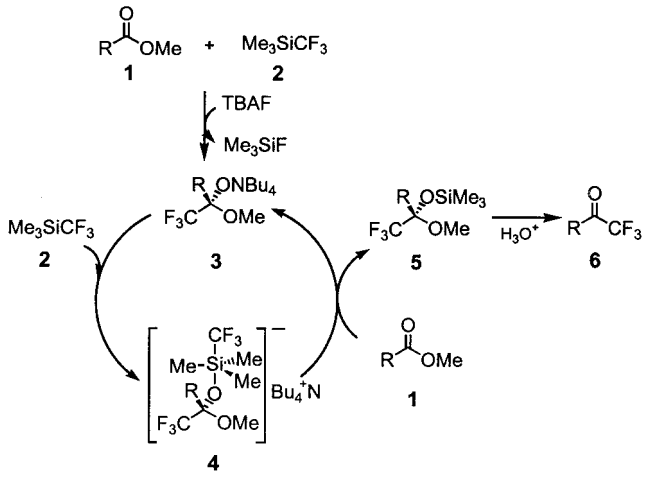
The mechanism for TMS-CF_3 addition is shown in Scheme 1. In the initiation step of the nucleophilic trifluoromethylation, TBAF reacts with TMS-CF_3 to transfer a CF_3 group to the ester. This gives rise to the deprotonated hemiacetal **3**, the true catalytic species. The latter in turn



Scheme 1. Proposed mechanism for the fluoride-induced nucleophilic trifluoromethylation of carboxylic esters with TMS-CF_3.

activates a second molecule of TMS-CF_3 through formation of a negatively charged pentacoordinated silicon species **4**, which transfers a CF_3 group to another ester molecule, resulting in formation of **5** and simultaneous regeneration of the catalytic species **3**.

However, when the initiator is added at higher temperatures (at or above 0 °C), **3** may decompose to give a methoxide ion, and the intermediate trifluoromethyl ketone, because of its high reactivity, may be subject to a second addition reaction.

In summary, we have developed a versatile method for the simple and efficient preparation of trifluoromethyl ketones from methyl esters.

Received: September 17, 1997 [Z10939IE]
German version: *Angew. Chem.* **1998**, 110, 880 – 881

Keywords: fluorine · ketones · nucleophilic additions · synthetic methods

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In Situ X-Ray Diffraction Study of the Initial Stages of Formation of MCM-41 in a Tubular Reactor**

Mika Lindén, Stephan A. Schunk, and Ferdi Schüth*

The successful preparation of MCM-41, a mesoporous silicate with hexagonally ordered cylindrical pores, has stimulated interest in this new class of composite materials since the pore sizes can be varied between 2 and 10 nm.[1, 2] Surfactants are used to induce the desired structure of the silicate polymer network. Usually, the synthesis of MCM-41 is carried out at surfactant concentrations at which the surfactant alone would not form a mesophase, which indicates a strong cooperative surfactant – silicate interaction. We describe here for the first time a continuous preparation of MCM-41 in a tubular reactor, which allows in situ X-ray diffraction (XRD) studies of the kinetics of mesophase formation on a mesoscopic length scale. The hexagonal mesophase is shown to form within the first three minutes of the reaction without passing through any intermediate phase. Different models have been developed to describe the formation of MCM-41. Beck et al.[2] proposed several possible pathways for the formation of such materials, and a more detailed, mechanistic model was presented by Monnier et al.[3] to account for the observation of an intermediate layered phase prior to reaching the hexagonal phase. This model introduced multidentate binding of silicate oligomers, preferred polymerization of silicate at the surfactant – silicate interface, and charge density matching as key factors in the formation of a surfactant – silicate mesophase. However, owing to the large number of different synthesis routes reported, each varying with respect to the silica source, surfactant concentration, pH, and the acid/base used etc., some of the reaction steps involved in the formation of the mesophase may differ depending on the applied experimental conditions. This is particularly important when organic precursors, such as tetraethoxysilane (TEOS), are used as the silica source, since their solubilities in aqueous solution are limited and therefore formation of an oil-in-water emulsion is expected as the initial reaction step. We describe here the results obtained by time-resolved in situ XRD measurements on the kinetics of formation of the hexagonal composite mesophase of such a system.

The reaction is too fast to allow data accumulation times long enough to obtain accurate kinetic data with a traditional setup for the investigation of liquids. To circumvent this problem, a tubular reactor was constructed and connected to a cell especially designed for XRD measurements of liquids; this allowed data accumulation times long enough to obtain a

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[**] This work was supported by the EU project ERB-FMRX-CT96-0084.

good signal-to-noise ratio and allowed the reaction time to be varied. The experimental setup is shown schematically in Figure 1. Two peristaltic pumps are used to control the ratio of

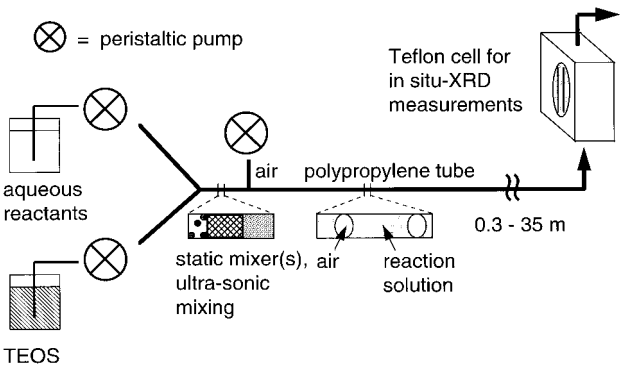

Figure 1. Schematic description of the tubular reactor setup. See Experimental Section for more details.

the aqueous to the hydrophobic reactants. TEOS is mixed with the aqueous solution, this solution is homogenized in an ultrasonic bath, passed through a series of static mixers, and subsequently passed through a tube ($\varnothing = 4$ mm) at a constant flow rate. The residence time of the reactants in the mixing step was 5–10 seconds. After mixing, air bubbles were introduced to prevent back-mixing in the tube; this resulted in approximately 20-cm-long trains of reaction solution separated by 3 cm of air. The residence time in the tube, that is the reaction time, is determined by the tube length. To ensure a good mixing of the reagents a small amount of *n*-butanol (BuOH) (BuOH:cetyltrimethylammonium bromide (CTAB) 1:4 w/w) was added to the aqueous solution. In order to exclude errors in the measured diffractograms, which arise from solid formation on the cell windows, data were accumulated for 4–10 minutes after which the reactor was flushed with distilled water and a background diffractogram was recorded. The background was then substracted from the original diffractogram. The experiment was repeated to give a total data accumulation time of 40 minutes. Fouling on the cell windows was detected mainly at short residence times (< 2 min), which was attributed to partial hydrolysis of TEOS; however, it never accounted for more than 15% of the measured signal. The reactor was cleaned prior to performing the next run by flushing with 0.2 M NaOH followed by large amounts of distilled water. The measured XRD patterns after different reaction times are shown in Figure 2. No peaks were observed for the pure surfactant solution, as expected for an isotropic micellar solution possessing no long-range order. However, a small-angle Bragg reflection appeared in the diffractogram upon addition of TEOS. The intensity of this reflection increased at longer reaction times due to the higher solid content of the solution. After a reaction time of only three minutes, two high-order peaks were resolved and indexed by assuming a hexagonal symmetry. No intermediate lamellar phase was detected. The solid product obtained after a reaction time of three minutes was immediately filtered and washed with water for further characterzation. The d_{100} spacing of 4.43 nm observed in the in situ measurements decreased to 4.0 nm upon drying at 90 °C (Figure 3). This

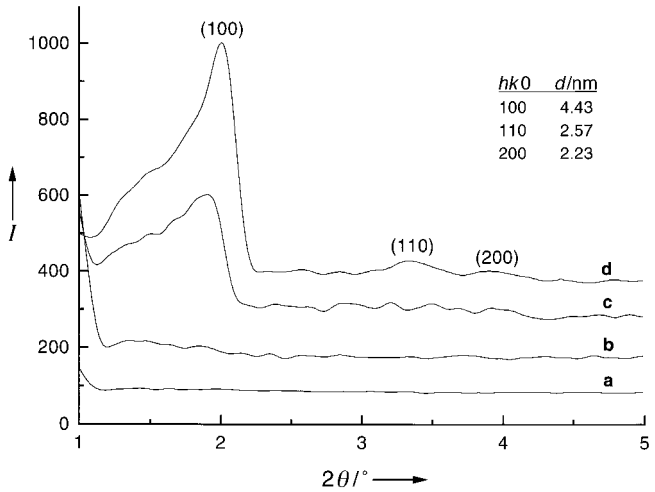

Figure 2. In situ XRD patterns of MCM-41 prepared in the tubular reactor in different reaction times. a) No added TEOS; after reaction times of b) 15 s, c) 90 s, and d) 180 s.

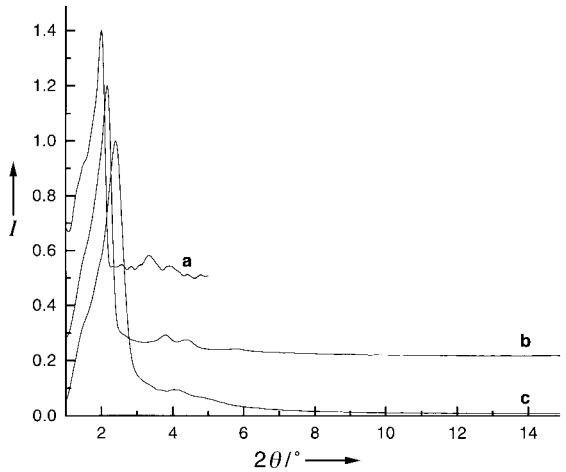

Figure 3. XRD patterns of MCM-41 prepared in the tubular reactor. a) In situ, reaction time 180 s, b) product isolated after 180 s and dried at 90 °C for 8 h, c) same sample as in b) but calcined at 550 °C for 6 h.

suggests that the wet sample was only partly condensed and that the removal of free and hydration water from the silicate–surfactant phase upon drying caused deswelling of the structure. These results are in good agreement with those presented in a recent study in which small-angle X-ray scattering (SAXS, ex situ) and EPR experiments were performed to study the formation of MCM-41.[4] The d_{100} spacing decreased further to 3.7 nm upon calcination at 550 °C. The XRD patterns of the dried and calcined product isolated after three minutes in the tubular reactor were identical to those obtained for the corresponding product prepared under stirring in an open beaker for one hour. This suggests that the mesostructure was more or less fully developed already at this stage although less condensed than the product prepared in an open beaker. Upon addition of TEOS the pH of the reaction solution decreased from 11.1 to 10.3, because of the presence of HCl traces in the TEOS solution and the formation of charged hydrolysis products. At this pH a variety of silicate species is known to form, ranging from monomers and dimers to oligomeric species with

  1433-7851/98/3706-0822 $ 17.50+.50/0

different charges.[5] It is well known that oppositely charged polyions are preferentially adsorbed on to interfaces of charged surfactant assemblies.[6] Furthermore, since the TEOS droplets are presumably covered by the surfactant, the concentration of hydrolysis products close to the surfactant–water interface will be very high. However, polymerization of silicate species adsorbed on to the surfactant headgroups will also readily occur at this pH at a rate higher than in the bulk.[3] This makes it almost impossible to determine whether certain species are preferentially adsorbed at the micellar interface. However, it is most probable that the reason for the rapid formation of the hexagonal mesophase observed in this study is caused by strong cooperative adsorption of polyionic silicate oligomers, which induce the hexagonal ordering of the composite assemblies.

N_2-sorption measurements at 77 K were carried out to compare the pore system of the product isolated from the tubular reactor (denoted as MCM-41t) to that of the product of the batch reaction (denoted as MCM-41b). The XRD patterns were identical for both samples. In both cases a fully reversible type IV isotherm was observed, which is characteristic for MCM-41 materials (Figure 4). The adsorbed volume

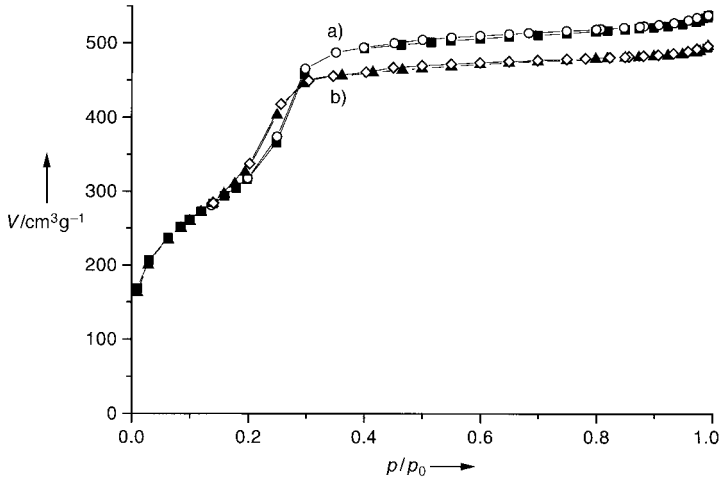

Figure 4. N_2-sorption isotherms of MCM-41 a) prepared as a batch synthesis in an open beaker, reaction time 60 min and b) prepared in the tubular reactor and isolated after 180 s.

increases linearly at low values of the relative pressure and then, because of secondary micropore filling inside the mesopores, it increases sharply between $p/p_o \approx 0.20-0.28$ for MCM-41t and 0.22–0.29 for the MCM-41b. The shift towards lower p/p_o values in the position of the sharp increase in the adsorption for MCM-41t compared to that for MCM-41b suggests that the pore diameter was slightly smaller for this sample. Pore sizes are difficult to calculate from the isotherms, since no good algorithms are available so far for this type of isotherm; however, the pore sizes are estimated to be around 2–3 nm.

In conclusion, we have for the first time carried out a continuous preparation of MCM-41 in a tubular reactor, which allows accurate in situ XRD measurements of the kinetics of formation of the hexagonal surfactant–silicate mesophase. The hexagonal phase was developed already after a reaction time of three minutes. In addition, the setup with a tubular reactor and an in situ XRD cell, which was developed to study fast processes with "slow" analytical techniques, may be used for other studies. Other analytical cells, like UV/Vis or Raman cells can be used, and there are few limitations with respect to the systems that can be studied. The concept introduced may thus be useful in a more general way.

Experimental Section

The composition of the reaction mixture by weight was: H_2O:NH_3 (25 wt %):CTAB:1-butanol:TEOS = 400:40:8:2:31. All experiments were carried out at 30 ± 2 °C.

Two Ismatec MCP peristaltic pumps were used to control the flow of the aqueous and the organic solutions in the tubular reactor. The tube was made of polypropylene with an inner diameter of 4 mm. The static mixing element was a stainless steel mixer (Sulzer, Switzerland) with five mixing elements of type SMXS DN 6. The XRD cell was built in house and consists of a Teflon body and PEEK (polyether ether ketone) windows (Goodfellow, 0.025 mm). The sample thickness between the polymer foils was 3 mm. Since the system was not optimized for the production of large amounts of product, the maximum running time before the reactor had to be cleaned was 15 min.

A STOE STADIP transmission X-ray diffractometer with a position sensitive detector (PSD) was used for all XRD experiments. For the in situ experiments data was accumulated between 0 and 6° (2θ). An ASAP 2010 (Micromeritics) sorptometer was used for the N_2-sorption measurements.

Received: July 8, 1997 [Z10650IE]
German version: *Angew. Chem.* **1998**, *110*, 871–873

Keywords: mesophases · mesoporosity · silicon · X-ray scattering · zeolite analogues

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