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Synchrotron-Based Method for the Study of Crystallization: Templated Formation of CoALPO-5 Catalyst

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Measurements that are experimentally demanding with conventional laboratory-based X-ray sources often become readily accessible when carried out with synchrotron radiation. This is so in the study of structural changes in solid catalysts under operating conditions.[1] It is also true in the study of the nucleation and growth of crystals from solutions, melts, and gels. With photon fluxes from a typical synchrotron exit port of the order of 10^{13} s^{-1} and, more importantly, with high-energy X-rays (up to 140 keV) capable of penetrating stainless steel containers, it is relatively straightforward to study condensed phases using appropriate high-temperature and/or high-pressure cells without serious attenuation in the intensity. Moreover, taking advantage of solid-state detectors, the white radiation of synchrotrons permits the rapid buildup of time-resolved diffraction patterns (under isothermal conditions) that allows the ready tracking of structural change occurring in a cell that is held in a fixed position. Figure 1a shows the energy-dispersive X-ray diffraction (EDXRD) geometry[2] available on station 16.4 at the 2 GeV Daresbury Synchrotron Radiation Source. The EDXRD facility is illuminated with radiation from a 6 T superconducting wiggler. The stainless steel autoclave shown in the figure can be operated up to temperatures of ca. 250 °C, permitting the in situ characterization during hydrothermal synthesis of most of the zeolitic materials. The solid-state detector is inclined at a fixed 2Θ angle chosen so that, from the photon energies available (7−140 keV), representative crystallographic spacings for zeolite structures are readily identifiable. With SRS electron beam currents of around 200 mA energy-dispersed patterns were integrated every 2 min in order to achieve adequate statistics for phase identification and the recording of reaction kinetics for the synthesis rates encountered here.

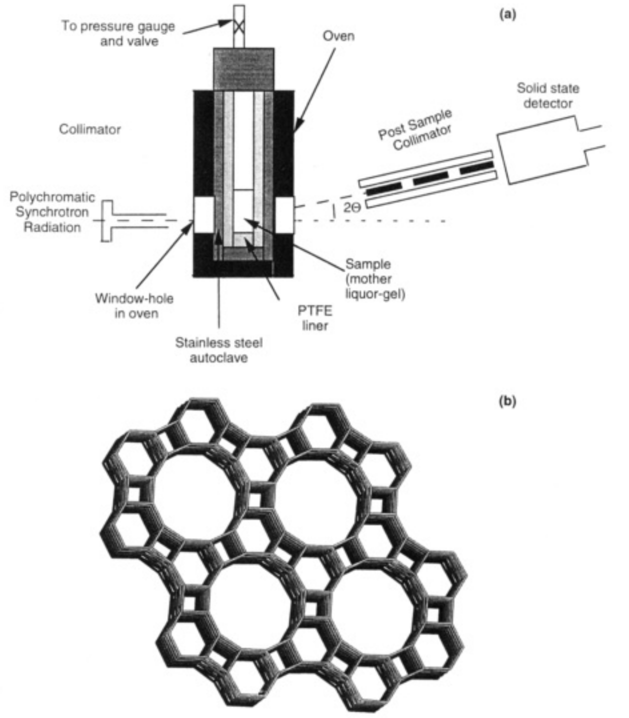

Figure 1. (a) Schematic diagram of the experimental setup for energy-dispersive X-ray diffraction. Synthesis takes place in the heated stainless steel autoclave and the crystallization is detected with a single-element (Canberra) Ge solid-state detector. This is inclined at a fixed 2Θ angle of 1.4556 ± 0.0001° and calibrated using NBS 640b Si. The integration time for each frame is 2 min. (b) Projection of framework of AFI structure. The vertices of the polyhedra are the T sites, which, in the ALPO-5 structure, are tenanted alternately by Al and P. Some of the Al^{3+} ions are replaced by Co^{2+} in CoALPO-5. In the crystallized products, molecules of triethylamine occupy the large channels as templates.

As part of a continuing program (see for example refs 3−6) of in situ studies of solid catalysts, catalyst precursors, and supports, we have recently focused on the growth and stability of open-structure aluminum phosphates (ALPOs) and their framework-containing, metal-substituted analogues (MeALPOs), which are promising catalysts for selective conversions of alkanes and alkanols.[7−9] Figure 1b illustrates the framework structure of the AFI structure common to ALPO-5 and MeALPO-5 considered in this communication. Formation of both MeALPOs and ALPOs is profoundly governed by the correct choice of organic nitrogenous templates; and although NMR, FTIR, and Raman spectroscopic studies (generally of the template) have shed[10] some light on the siting and state of the organic species inside the growing cages and channels, there is need for additional techniques (apart from small-angle and wide-angle X-ray-scattering[11] and light-scattering[12,13] techniques) capable of tracking the dynamics of crystal nucleation and growth in the presence of the

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template. Valuable insights into template-mediated crystallization of zeolites may also be achieved using small-angle neutron-scattering studies.[14] Conventional X-ray diffraction studies of the kinetics of crystallization of zeolites and ALPO's have, in general, to be conducted ex situ by withdrawing the crystalline products at regular intervals; the intensities are usually too low to permit in situ studies (but see ref 15). The advantage of in situ studies using synchrotron radiation is that it readily permits time resolution and also offers the opportunity to characterize intermediate phases which are structurally significant and stable only at high temperatures. The study illustrated here, like recent comparable ones,[16,17] may be straightforwardly adapted for the investigation of a variety of other materials and systems including high-temperature, solid-state (phase) transitions.[18]

Stacked diffraction plots as a function of time for the appearance of ALPO-5 (Figure 1b) at 165 °C from a mother liquor containing $1.0Al(OH)_3$:$1.5H_3PO_4$:$0.8NEt_3$:$30H_2O$ are shown in Figure 2a. After an induction period of about 20 min (which is probably due partly to the buildup of pressure and partly to nucleation) the crystallization begins at a rapid rate. The ALPO-5 appears in a both stable and phase pure state. Typically, the intensities of the reflections attain saturation within ca. 15 min and remains nearly constant. When the mother liquor contains cobalt (the precise composition being $0.04Co(Ac)_2$:$0.96Al(OH)_3$:$1.5H_3PO_4$:$0.8NEt_3$:$30H_2O$), however, the stacked time lapse diffraction patterns are quite different (Figure 2b). Note that, after an induction period comparable to that of ALPO-5, the CoALPO-5 crystallization begins and simultaneously another intermediate phase, identified as a chabazite (CHA) related structure, starts to appear and disappear slowly (depending on the temperature) giving finally only pure CoALPO-5. These observations are in line with those of Uytterhoeven and Schoonheydt[19] and others who report a tendency of the parallel formation of ALPO-5 and chabazite structures depending on template concentration. Although the disappearance of the reflections of the CHA phase takes a very long time at lower temperatures (<195 °C), the synthesis carried out at 195 °C clearly showed this process occurs above ca. 55 min. We do not observe this intermediate phase during the in situ ALPO-5 synthesis, as discussed above. Details of the kinetics of these processes will be reported elsewhere.

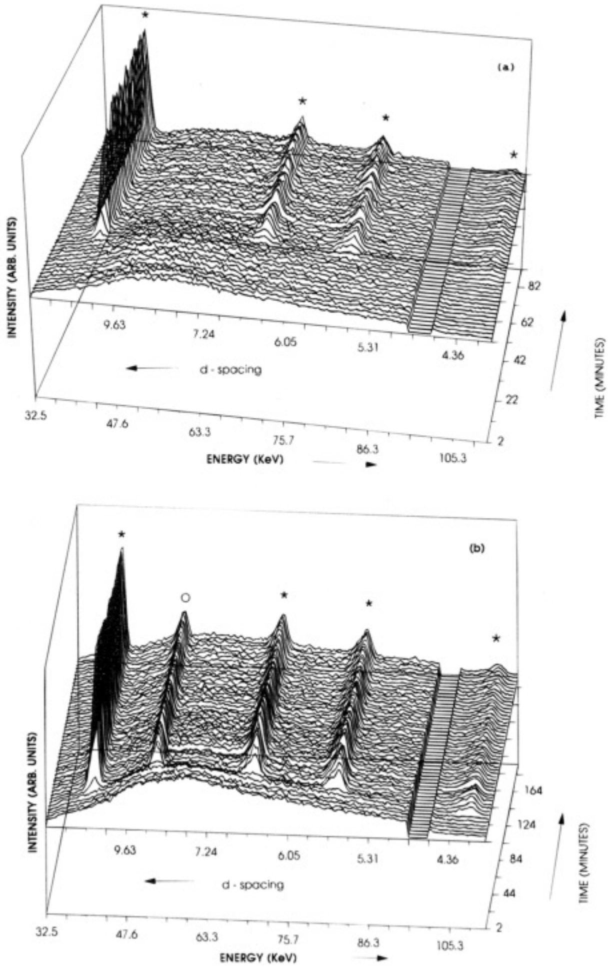

Figure 2. Time-resolved X-ray diffraction patterns of (a) ALPO-5 and (b) CoALPO-5, collected at 165 °C. Energies and *d*-spacing to which they correspond (at the fixed angle 2Θ) are plotted on abscissa. Note the structureless diffraction patterns from 2 to ca. 20 min signifying the mother liquor–gel phase. The reflection at 98.8 keV due to the autoclave has been excluded from the figure for clarity. The reflections due to the AFI structure are denoted by asterisks, while the open circle relates to the CHA structure. The other reflections associated with the CHA phase are much weaker in the EDXRD patterns but have been identified in separate ex situ angle resolved experiments.

The technique described here is an extension of the "fixed cell" geometry used earlier by us[20] in the in situ energy-dispersive X-ray diffraction study of natural gas conversion by CO_2 reforming, where rare earth iridate and ruthenate pyrochlores were structurally tracked up to 1000 K and by Barnes et al. in condensed systems.[16,17] Only a minor adaptation of our technique is required to make it suitable for studying other templated systems (e.g., urea and thiourea channel complexes or metalloenzymes). The technique outlined herein has proved helpful in elucidating the kinetics of formation of other zeolites, which is to be the subject of a paper to be published elsewhere.

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