We have developed a procedure for the synthesis of thin zeolite films that does neither require hydrothermal heating during the crystallization process nor a subsequent calcination step. A combination of spin-coating and hydrothermal synthesis techniques was employed for the preparation of thin zeolite films on 2D substrates. The goal of this work was to study the characteristic features of zeolite A films synthesized on noble metal substrates under ambient conditions. The structural properties of the zeolite A and the effect of the synthesis parameters on the formation of zeolite films were studied by grazing incidence X-ray diffraction performed at the ID01 beamline. A well-defined X-ray beam (wavelength λ = 0.156 nm) strikes the sample surface under a small incident angle (α_i) close to the critical angle (α_c) for total external reflection, typically some tenths of a degree. The scattered intensity was collected by a CCD camera and a position sensitive detector (PSD) placed perpendicular to the sample surface.

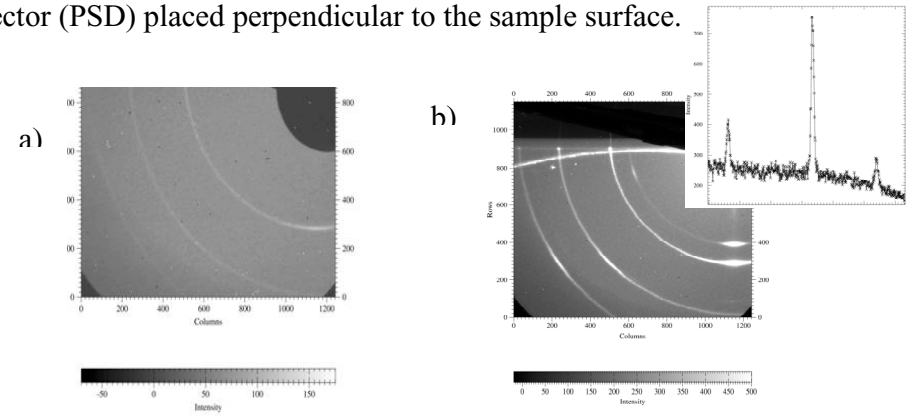

Figure 1. CCD images of the spin-coated zeolite A layer prior to crystal growth (a) and (b) after five days of room temperature synthesis.

Another colloidal system containing aluminophosphates ($AlPO_4$-18) with a structure built of AlO_4- and PO_4-tetrahedral units was investigated with an *in-situ* cell. The mechanism of film formation is discussed based on the results obtained from the crystals growing randomly in the solution and on two-dimensional supports. The synthesis of pure siliceous hydrophobic zeolite BETA from colloidal precursor solutions, and the preparation of ultra-thin films on silicon wafers *via* spin-coating of stable BETA/EtOH colloidal suspensions was carried out in a specially designed reactor. XRD patterns of the films were recorded at a constant incident angle α_i=0.1° which corresponds to a penetration depth of about 8 nm. The XRD pattern obtained from the BETA film contains very intensive Bragg reflections with *(hkl)* values equal to *(101), (205)* and *(116*) (Fig. 2 b,c). GID X-ray radiation allows for an investigation of the very thin polycrystalline zeolite films and their average particle size.

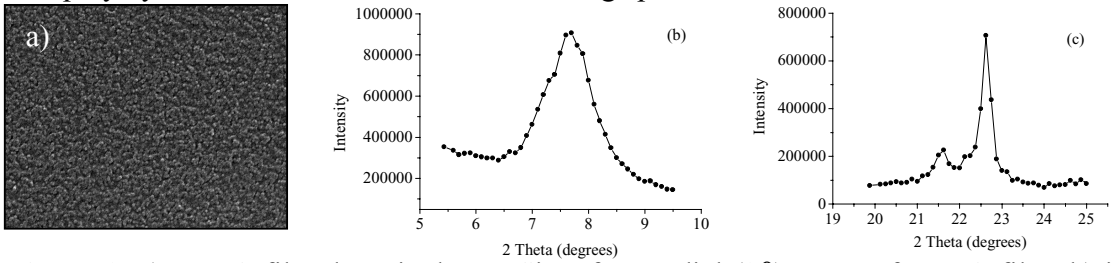

Figure 2. a) BETA film deposited on a Si wafer; Radial (2θ)-scans of BETA film: b) in the 2θ range 5-10°, c) in the 2θ range 19-25° (α_i=0.1°).

The synthesis of stable coating solutions containing MFI nanocrystals and the preparation of composite films possessing both micro/mesoporosity on planar substrates *via* evaporation-induced self-assembly of precursor acidic silica/CTABr/ethanol solutions mixed with stable MFI/ethanol colloidal suspensions was investigated. The intensity of Bragg peaks at 1.87° (mesoporous peak) and 7.94° (MFI peak) as a function of the incident angles for the pure MFI, mesoporous and a composite film was collected. A shift in the maximum intensity towards higher incident angles is measured for the composite film; this indicates increased density in comparison to the pure mesoporous, and pure MFI films, as detailed below.

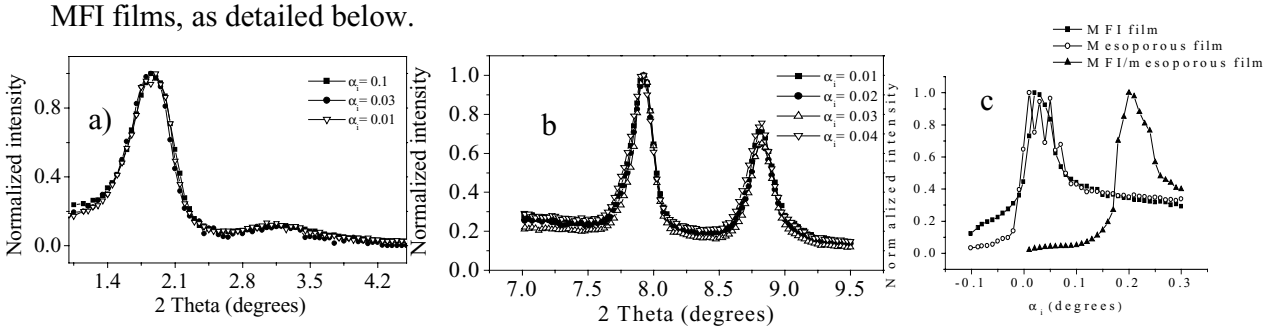

Figure 3. Radial 2θ-scans of calcined micro/mesoporous composite film in the a) 1.0-4.5° and b) 6.5-10.0° 2θ ranges; c) the α_i- dependent intensity distribution for MFI (7.94° 2θ), mesoporous (1.87° 2θ) and MFI/mesoporous composite (7.94° 2θ) films.

Depth-dependent structural information on a certain lattice plane is obtained by keeping the corresponding $2\theta_{(hkl)}$ constant and varying α_i. The intensity of Bragg peaks at 1.87° (mesoporous peak) and 7.94° (MFI peak) as a function of the incident angle for the samples is depicted in Figure 3c. Since the density of a layer is related to the position of the critical angle, the multiple maxima found for sample MCM indicate depth-fluctuation in the layer density, corresponding to angles between 0.01° and 0.1°. A similar measurement for MFI sample shows a more even distribution of the intensity as a function of α_i with pronounced maxima at the critical angle (α_c = 0.05°). This curve is characteristic for single crystals, where all lattice planes of the corresponding Bragg peak are oriented perpendicular to the substrate, thus G^1_{hkl} is placed parallel to the sample surface. Surprisingly, the intensity distribution in the same α_i region for the MFI/mesoporous composite film shows a shift in the maximum intensity towards higher incident angles. This indicates increased density of the deposited layer in comparison to the pure mesoporous and pure MFI films.

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