Zeolite Beta Films Assembled via the Langmuir-Blodgett Technique

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Introduction

There is a continuous interest in the development of methods for the preparation of zeolite films and layers and although such materials have been studied for a number of emerging applications, traditional areas of zeolite application such as separation and catalysis remain to be the main subject of works published [1]. Different techniques have been developed to assemble zeolite crystals onto flat supports. The crystals then serve as seeds for zeolite film growth and in many cases control the continuity and orientation of films obtained. There are many examples of applications of the sole assembled crystals without subsequent secondary growth. The aim of the present work is to explore the Langmuir-Blodgett (LB) method for preparation of LB zeolite films.

Materials and Methods

Two zeolite Beta samples were prepared from synthesis mixtures with the molar composition $0.31Na_2O$:9TEAOH:$0.5Al_2O_3$:$25SiO_2$:$489H_2O$ (referred in the text as colloidal Beta) and $1.0SiO_2$:$0.03Al_2O_3$:0.60TEAOH:0.60HF:$5.0H_2O$ (large crystal Beta) by hydrothermal treatment at 90 and 150 ºC for 19 and 21 days, respectively. The colloidal Beta was purified by three times centrifugation and re-dispersion in methanol. 0.7 mM cetyltrimethylammonium bromide (CTAB) was added to the final methanol suspension containing 1 wt% zeolite. The large crystal Beta was recovered by filtration and dispersed in methanol or chloroform to obtain 1, 3 or 5 wt% zeolite concentrations. The methanol or chloroform zeolite suspensions were spread at the air-water interface in a LB trough (NIMA 1232D1D2) using a compression speed of 50 cm^2 min^{-1}. The floating films were transferred to silicon wafers (pre-cleaned with acetone and 2-propanol) at a surface pressure of 10 mN m^{-1} and a dip speed of 1 mm min^{-1}. The zeolite Beta samples and LB films were characterized by X-ray diffraction (XRD), Dynamic Light Scattering (DLS), Scanning Electron Microscopy (SEM), Thermogravimetry (TG), Attenuated Total Reflection Infrared Spectroscopy (ATR IR) and chemical analysis.

Results and Discussion

The size of the CTAB-modified colloidal Beta from DLS measurements was about 180 nm, whereas according to SEM, the average particle size of the large crystal Beta was ca. 1 µm. The large crystal Beta was synthesized in fluoride media and thus hydrophobic while the colloidal nature of the colloidal Beta imposed increased hydrophilicity, which was confirmed by the weight loss up to 150ºC measured by TG; about 1 wt% for the large crystal Beta and 6 wt% for the colloidal Beta. LB films of high quality extending over the substrate area used for film deposition could be prepared using both zeolite samples (Fig. 1). However, different suspensions were used to prepare the films. Surfactant was added to the colloidal Beta dispersed in methanol in order to form a film at the air-water interface, which was not necessary for the large crystal Beta. Both methanol and chloroform were used as a dispersion medium for the large crystal Beta and, according to SEM, the morphology of the LB films prepared was similar. However, a larger amount of sample was used from methanol dispersions, e.g., for 3 wt% zeolite, the solution spread in the trough was 1000 µl from methanol and 500 µl from chloroform dispersions. Visual and SEM examination showed that the films were very homogeneous, generally of monolayer characteristics and the films prepared from colloidal Beta were denser compared to the large crystal Beta films, for which larger bare substrate areas between the crystals can be seen (Fig. 1). The latter is related to the different morphology of the crystals. The high crystallinity of the LB zeolite films was confirmed by XRD and ATR-IR. Samples composed of a large crystal Beta LB film deposited on top of colloidal Beta LB film were also prepared.

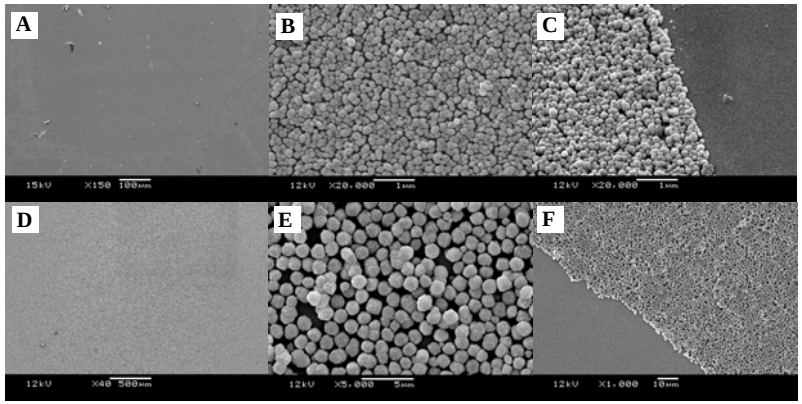

Figure 1. SEM images of Langmuir-Blodgett zeolite Beta films prepared from A-C) colloidal Beta and D-F) large crystal Beta.

Significance

Langmuir-Blodgett films of high quality were prepared from two zeolite Beta samples having different crystal size and morphology and different hydrophobic/hydrophilic properties. This result suggests that the Langmuir-Blodgett technique can be used to prepare LB films from different zeolite systems by adjusting the experimental parameters. Considering the fact that preformed crystals are used, the crystal morphology can be carefully selected and thus the morphology of the LB films can be predicted. The method can also be used to prepare multi-layers of different zeolites.

References

1. Coronas, J. and Santamaria, J. *Topics Catal.* 29, 29 (2004).