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Synthesis of mono- and bi-layer zeolite films on alumina substrates

Synthèse de films zéolithiques mono- et bicouches sur des substrats d'alumine

Ali Said [a, b], Habiba Nouali [a], Lionel Limousy [a], Patrick Dutournié [a], Ludovic Josien [a], Joumana Toufaily [b], Tayssir Hamieh [b], T. Jean Daou [a, *]

[a] *Université de Haute Alsace (UHA), CNRS, Equipe Matériaux à Porosité Contrôlée (MPC), Institut de Science des Matériaux de Mulhouse (IS2M), UMR 7361, ENSCMu, 3 bis rue Alfred Werner, 68093 Mulhouse, France*

[b] *Laboratory of Materials, Catalysis, Environment and Analytical Methods, Faculty of Sciences, Doctorate School of Science and Technology, Lebanese University, Lebanon*

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ABSTRACT

Bilayer zeolite films ZSM-5/ZSM-5, ZSM-5/EMC-1 and NaY/ZSM-5 were synthesized on α-alumina plates. The bottom ZSM-5 or faujasite Y (NaY) zeolite layers were obtained by direct hydrothermal synthesis or by using a seeding step followed by a secondary growth method, respectively, while the secondary growth method was used for the synthesis of all the top zeolite layers. A complete characterization of the obtained materials is proposed using various techniques, such as X-ray diffraction, scanning electron microscopy, X-ray fluorescence and nitrogen sorption measurements. Continuous and highly crystallized bi-layer zeolite films with thicknesses around 11–18 μm were obtained.

RÉSUMÉ

Des films composés de deux couches zéolithiques ZSM-5/ZSM-5, ZSM-5/EMC-1 et NaY/ZSM-5 ont été synthétisés sur des plaques en α-alumine. Les couches inférieures de zéolithes ZSM-5 ou de faujasite Y (NaY) ont été obtenues respectivement par synthèse hydrothermale directe ou par la méthode d'ensemencement suivie d'une étape de croissance secondaire, tandis que la méthode de croissance secondaire a été privilégiée pour la synthèse de toutes les couches supérieures de zéolithes. Une caractérisation complète des matériaux obtenus est proposée en utilisant diverses techniques, telles que la diffraction de rayons X, la microscopie électronique à balayage, la fluorescence des rayons X et des mesures de manométrie de sorption d'azote. Des films composés de deux couches zéolithiques hautement cristallisés avec une épaisseur variant entre 11 et 18 μm ont été obtenus.

* Corresponding author.
E-mail addresses: ali.said@uha.fr (A. Said), habiba.nouali@uha.fr (H. Nouali), lionel.limousy@uha.fr (L. Limousy), patrick.dutournie@uha.fr (P. Dutournié), ludovic.josien@uha.fr (L. Josien), joumana.toufaily@ul.edu.lb (J. Toufaily), tayssir.hamieh@ul.edu.lb (T. Hamieh), jean.daou@uha.fr (T.J. Daou).

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1. Introduction

Due to the manifold applications of crystalline zeolites, increasing attention worldwide has been paid to the preparation of zeolites in forms suitable for practical utilization and to the development of methods for producing zeolite objects (films, membranes, pellets, microspheres …) with controllable thicknesses. Among these zeolite objects, supported zeolite layers have great potential and great utilities and their functions and application can be easily tuned by changing the zeolite species used to generate them. Zeolite films and membranes are believed to be important materials in the technology era with novel emerging applications in various fields such as membrane separation [1,2], catalysis [3–5], chemical sensors [6,7], anti-microbial coating [8,9], microelectronic devices [10–13] and corrosion resistance [14–16].

Efforts have been devoted to the development of different methods for the synthesis of supported zeolite films such as in-situ crystallization and pre-seeding with regrowth or sticking of nanocrystals on a surface [2]. In-situ crystallization can be realized in a traditional liquid phase [1,17,18], by solid state transformation [19] or microwave-assisted hydrothermal synthesis [20] while pre-seeding methods were achieved in alkaline [21] and fluoride [22] routes. The vapor phase transport method was also used for the synthesis of MFI (Mobil Five) membranes [23]. But unfortunately, most of the efforts focused on the study of single-layered zeolite film/membranes composed of one type of zeolite. If zeolitic materials are selective in size and shape and display various relevant properties depending on their nature or chemical composition, the combination of different zeolites might be a wise solution to enhance some industrial applications. As a consequence, two-layered films of different zeolites were developed to improve the efficiency of separation membranes [24–26] or to combine the extreme properties of microporous materials. For example, the development of methods to produce bi-layer zeolite films composed of high and low silica zeolites on aluminum substrates were done by our team in order to reduce the molecular contamination in satellites [27–30]. In those bi-layer films, the bottom layer is represented by the ZSM-5 (Zeolite Socony Mobile 5) (MFI structure type) zeolite while EMC-1 (Elf Mulhouse Chemistry 1) zeolite (FAU (faujasite) structure type) or EMC-2 (Elf Mulhouse Chemistry 2) zeolite (EMT (Elf Mulhouse Chemistry Two) structure type) or beta zeolite forms the top layer of the material [27–30]. In this paper MFI-type zeolites and FAU-type zeolites are highlighted due to their great potential for industrial applications.

The MFI structure type is characterized by a porous system formed by the interconnection of straight circular channels (5.4 Å × 5.6 Å) with sinusoidal and elliptical channels (5.1 Å × 5.4 Å) which is very interesting for some environmental applications such as the removal and/or remediation of anions in water [31] and volatile organic compounds (VOCs) [32–34]. Depending on the silicon to aluminum molar ratio of the microporous framework, ZSM-5 (Si/Al < 500) and silicalite-1 (Si/Al > 500) are two zeolites presenting the MFI structure [33–37].

FAU-type zeolite is of particular interest due to its high aluminum content, i.e. its hydrophilicity. Its pores are composed of supercages, with a free diameter of 11.6 Å, interconnected through circular 12-member-ring (MR) apertures with a diameter of 7.4 Å [38].

Conventional NaY zeolite (FAU-structure type) presents a silicon-to-aluminum molar ratio between 1.5 and 2.5. High silica FAU-type zeolite, with a silicon to aluminum molar ratio between 3 and 5, can be synthesized directly by using specific structure-directing agents (SDAs) in a synthesis hydrogel. Thus, Guth and co-workers reported the crystallization of a high silica FAU-type zeolite commonly named EMC-1 (Elf Mulhouse Chemistry One) by using the 15-crown-5 ether as SDA [38–41].

Consequently, the scope of the present work was to produce zeolite bi-layered films composed of high (ZSM-5 zeolite) and low (EMC-1 and NaY zeolites) silica zeolites on alumina plates as represented in Fig. 1. Three different zeolite bi-layered films were synthesized, ZSM-5/ZSM-5, ZSM-5/EMC-1 and NaY/ZSM-5. The crystallinity, homogeneity, thickness and Si/Al molar ratio of the both layers as well as other microstructural properties are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray fluorescence (XRF) and nitrogen sorption measurements. The weight of the zeolite layer was also estimated by nitrogen sorption measurements using the method of mass assessment.

2. Experimental section

2.1. Materials

The chemical reagents used in this work were aluminum powder (99.95 wt %, Aldrich), sodium hydroxide (NaOH, 99.99 wt %, Aldrich), tetraethylorthosilicate (TEOS, 98 wt %, Aldrich), tetrapropylammonium hydroxide (TPAOH, 40 wt %, aqueous solution, Aldrich), aluminum isopropoxide (98 wt %, Aldrich), colloidal silica (Ludox HS-40, Aldrich), tetramethylammonium hydroxide pentahydrate (TMAOH, $5H_2O$, 98 wt %, Alfa Aesar), sodium aluminate (57 wt % Al_2O_3, 40 wt % Na_2O, Strem Chemicals), 15-crown-5 (98 wt %, Alfa Aesar) sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$ > 98%, Sigma) with aluminum sulfate-18-hydrate ($Al_2(SO_4)_3$, Aldrich), ethanol and distilled water. All the chemical reagents were of analytical grade.

Pieces of 2 × 2 cm^2 of alumina (0.2 cm thick) were purchased from Final Matériaux Avancés (Wissembourg, France).

2.2. Pre-treatment of the substrates

2.2.1. Before synthesis of the bottom layer of ZSM-5 zeolite

Pre-treatment of the substrates was fully described in a previous paper [14,30] and consists of cleaning the plates in an aqueous solution of a detergent (Alconox, 3 g in 400 mL of distilled water) heated to 60 °C for 1 h [30, 32]. They were then rinsed with distilled water, dried at 70 °C and cooled down to ambient temperature.

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