Microporous and Mesoporous Materials 174 (2013) 154–162

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

# Combined silica sources to prepare preferentially oriented silicalite-1 layers on various supports

P. Hrabanek [a,*], A. Zikanova [a], J. Drahokoupil [b], O. Prokopova [a], L. Brabec [a], I. Jirka [a], M. Matejkova [a], V. Fila [c], O. de la Iglesia [d], M. Kocirik [a]

[a] J. Heyrovsky Institute of Physical Chemistry of the ASCR, v.v.i.,Dolejskova 2155/3, 18223 Prague 8, Czech Republic
[b] Institute of Physics of the ASCR, v.v.i.,Na Slovance 2, 18221 Prague 8, Czech Republic
[c] Institute of Chemical Technology Prague, Technicka 5, 16628 Prague 6 Dejvice, Czech Republic
[d] Centro Universitario de la Defensa, Academia General Militar, Ctra. de Huesca s/n 50090 Zaragoza, Spain

ARTICLE INFO

*Article history:*
Received 23 August 2012
Received in revised form 1 March 2013
Accepted 9 March 2013
Available online 16 March 2013

*Keywords:*
Zeolite
Synthesis
Orientation
Layer
Support

ABSTRACT

Direct *in-situ* hydrothermal synthesis was optimized via combination of monomeric (TEOS) and colloidal (TOSIL) silica sources to prepare preferentially *b*-oriented high silica MFI zeolite (silicalite-1) layers on different supports using conventional heating. Crystallographic Preferred Orientation (CPO) indices and our created Preferred Orientation Coverage (POC) values were used to determine preferred orientation and its surface coverage. Particle size distribution of precursor species was measured with Dynamic Light Scattering technique. Crystal intergrowth and zeolite phase purity were checked with Scanning Electron Microscope and X-ray diffraction. Solid and (*a* + *b*)-oriented self-supported silicalite-1 layers were synthesized on mercury surface at static and vibration conditions. Additional self-assembled and oriented silicalite-1 layers floating in bulk solution were prepared from solutions with enhanced silica content. Preferentially *b*-oriented silicalite-1 layers were prepared on silicon wafer and polished non-porous stainless steel. Partial *b*-orientation was achieved for polished porous stainless steel supports. Remarkably intergrown and *b*-oriented silicalite-1 layers were synthesized on porous stainless steel covered by $TiO_2$ layer that was impregnated with tetrabutylorthotitanate acting as a coupling agent and/or surface charge modifier.



## 1. Introduction

Development and optimization of synthesis procedures that would enable preparation of preferentially oriented MFI zeolite (ZSM-5 or silicalite-1) layers is a challenging topic. The oriented MFI zeolite layers were already synthesized on different supports and showed potential application in the fields of membranes [1–6], microreactors [7,8], sensors [9,10] and optoelectronic devices [11]. There are several reasons to control crystal size, external and internal crystal morphology and in particular crystal orientation in polycrystalline MFI zeolite layers. Due to diffusional anisotropy of MFI zeolite structure and crystal morphology, permeation through *c*-oriented layers is much less favorable in contrast with *a*- or *b*-oriented MFI zeolite monolayer membranes with access to sinusoidal and straight channels, respectively. For an intergrown polycrystalline layer, principal requirement is aimed on minimization of transcrystalline mass transport resistance to required penetrant. According to theoretical consideration of MFI zeolite membrane permeation, based on assumption that a polycrystalline layer can be synthesized as an assembly of intergrown monocrystals, the most favorable configuration would be a thin, fully intergrown *b*-oriented layer exhibiting higher fluxes compared to *a*, *c*- or randomly oriented layers. In such an ideal system, *b*-orientation of silicalite-1 crystals in a layer facilitates an easy access to the straight channels of MFI zeolite pore network and exhibits considerably higher contribution to transmembrane flux due to the anisotropy of intracrystalline diffusion. Crystal orientation is important with respect to MFI zeolite structure anisotropy reflected by an anisotropy factor of intracrystalline diffusion to permeating species inside MFI zeolite crystal. The anisotropy factor of intracrystalline diffusion was estimated for several permeating species by molecular dynamic computation [12], PFG NMR technique [13,14], random walk model [15] and sophisticated macroscopic technique [16].

Basic orientation of pore structure in MFI zeolite monocrystals, shown in Fig. 1, is as follows: *a*-oriented (100) – direct entrance to sinusoidal channels, *b*-oriented (010) – direct entrance to straight channels, *c*-oriented (001) – no entrance.

Based on several observations of MFI zeolite crystal growth, primary silicalite-1 crystals formed in bulk solution are adsorbed with their largest face (*b*-orientation) on support surface and grow into

* Corresponding author. Tel.: +420 266053626; fax: +420 286582307.
*E-mail address:* pavel.hrabanek@jh-inst.cas.cz (P. Hrabanek).

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http://dx.doi.org/10.1016/j.micromeso.2013.03.007

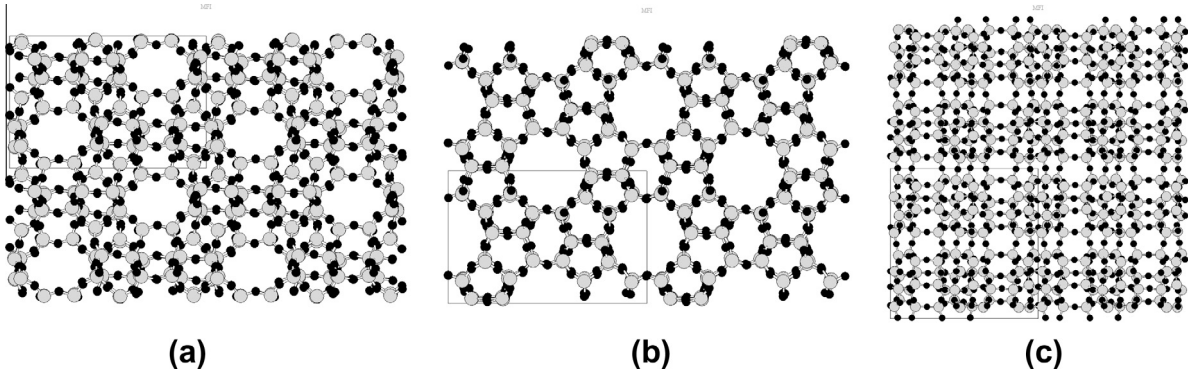


**Fig. 1.** Basic orientation of silicalite-1 framework, (a) (100) *a*-orientation, (b) (010) *b*-orientation, (c) (001) *c*-orientation.

thin films during an early stage of crystallization. After substantially prolonged crystallization period, platelike monocrystals grow into twinned intergrown coffin-shaped crystals [17] forming thick films [18] and opening a series of questions focused on the role of grain boundaries between individual subunits in MFI zeolite crystal twins. The grain boundaries may represent an internal barrier for intracrystalline diffusion across boundary [19–21] or be permeable along interface [22]. For an intergrown zeolite multilayer membrane, the impact of intracrystalline grain boundaries on mass transport would depend on boundary permeabilities in normal and tangential direction as well as on boundary orientation within a membrane (individual crystal orientation).

Preferential orientation of individual monocrystals and intercrystalline grain boundaries also essentially determine crack formation during removal of template decomposition products from polycrystalline layers [23,24], where different expansion/shrinkage properties of silicalite-1 along individual crystallographic axes are responsible. A detailed study performed on zeolite crystal beds and polycrystalline layers showed that template removal is represented by interplay between mobile template decomposition products and decomposition/association reactions establishing: (i) formation, (ii) location, (iii) chemical nature and (iv) stability of organic deposits/residua in a zeolite crystal layer [23–28] and finally zeolite membrane permeation and selectivity. Mixed (*a* + *b*)-oriented layer is more advantageous with respect to reduction of defects formed during template removal [29]. Defects in *c*-oriented silicalite-1 membranes were reported to be significantly eliminated by using Rapid Thermal Processing of as-synthesized membranes [30].

Different synthesis pathways have been reported in the literature to obtain oriented zeolite layers and films. The most frequent techniques are secondary crystal growth and one-step *in-situ* hydrothermal crystallization.

The secondary crystal growth technique uses defined colloidal zeolite seeds that are deposited on support surface. After zeolite seed deposition usually performed by dip or spin coating or electrophoretic deposition [31,32], classic *in-situ* hydrothermal synthesis proceeds to grow *b*-oriented [4] or *a*-oriented [33] MFI zeolite films and membranes. Disadvantage of secondary crystal growth lies in rather laborious character, starting from preparation of homogeneous colloidal MFI zeolite seeds followed by defined and uniform seed deposition and final hydrothermal growth that is also sensitive to many synthesis process parameters and conditions.

One-step direct *in-situ* hydrothermal crystallization is carried out without previous deposition of zeolite seeds on support surface [3] allowing possibility to easily coat any surface of complex geometrical objects (grains, grids, monoliths) that are important for practical applications. Disadvantage of one-step direct *in-situ* hydrothermal crystallization is also sensitivity to many synthesis process parameters and conditions usually coupled with longer crystallization period and support surface chemistry. Due to these facts, the one-step direct *in-situ* synthesis procedures have to be tailored made and optimized for each particular support. Recently, a dynamic method using a rotating convention oven was reported to reduce crystallization time to prepare oriented, uniform and continuous silicalite-1 layer on stainless steel substrates [34].

For practical application and process scale-up capability, primary aim of presented study was focused on elaboration of simple and direct one-step *in-situ* synthesis procedure. One of novel approaches, used in this study and introduced into one-step *in-situ* synthesis procedure, was specific combination of two silica sources strongly distinct in silica aggregation state. This phenomenon was discovered in our laboratory during a series of experiments with growth of self-supported silicalite-1 layers on mercury surface using simple synthesis procedure [35] that was modified in the present work via combination of different silica sources. A partial replacement of monomeric silica with a colloidal one led to improved crystal intergrowth and accelerated crystallization promoting preferential *b*-orientation of silicalite-1 crystals on mercury side of a layer. A similar phenomenon of improved crystal intergrowth was reported in the literature and explained by results obtained after addition of some Intergrowth Supporting Substances [36]. The principal aim of presented study was the application of this novel synthesis approach to prepare oriented zeolite layers on broad variety of supports which essentially differ in their softness, corrugation, texture, porosity and surface chemistry. During this study a need arose to elaborate more complex system of zeolite layer characteristics capable to describe in detail crystal orientation and layer continuity and their time development and dependence on synthesis conditions. As to our best knowledge, the system of characteristics proposed in the present study has not been used elsewhere.

## 2. Experimental

### 2.1. Synthesis of silicalite-1 layers

Silicalite-1 layers were hydrothermally synthesized on mercury (99.9995%, Sigma-Aldrich), silicon wafer (Tesla), non-porous (GoodFellow) and porous stainless steel (TRUMEM™) supports. Before each synthesis, support surface was ultrasonically purified in hydrogen peroxide solution (30%, Sigma–Aldrich) and rinsed with deionized water to remove contaminants except mercury that was clean with certified purity. Molar compositions of used synthesis solutions are shown in Table 1. Total molar composition of both silica sources was always kept constant and equal to 1.

Tetraethylorthosilicate (TEOS, puriss.; ⩾ 99%, Fluka) and colloidal $SiO_2$ (TOSIL, 30 wt.% suspension in water, KOMA s.r.o., Czech Republic) were used as silica sources. Tetrapropylammonium