Journal of Solid State Chemistry 181 (2008) 2469–2472

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Fabrication of oriented zeolite L monolayer via covalent molecular linkers

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ARTICLE INFO

Article history:
Received 20 February 2008
Received in revised form
6 June 2008
Accepted 11 June 2008
Available online 17 June 2008

Keywords:
Zeolite L
Oriented monolayer
Covalent molecular linker
Supramolecular organization

ABSTRACT

For the first time, 1,4-diisocyanatobutane (DICB) was used as the covalent molecular linker in this study to prepare the uniformly oriented zeolite L monolayer with relatively high coverage degree and close packing degree. This could be ascribed to substantial amounts of DICB self-assemble and standing on the substrate surface instead of folding up into a U-shape. This point has been further verified by the quality of oriented zoelite L monolayers obtained from the procedure involving DICB, 1, 4-bis (triethoxysilyl) benzene (BTSEB) and 1,2-bis(trimethoxysilyl)ethane (BTMSE) as covalent molecular linkers.

1. Introduction

Recently, the interest in organization of micrometer-sized zeolite crystals into uniformly oriented monolayers on various supports has greatly increased as new application fields have been envisaged [1–21]. The potential applications span a wide range of uses such as membranes, chemical sensors, low-*k* dielectrics, and hosts for supramolecular organization of guest molecules or nanostructures [6,10,22–29]. The preparation of close-packed monolayers of zeolite A was first realized by physical adsorption of the microcrystals onto a substrate [5]. This method was also used for realizing the first ship-in-a-bottle synthesis of luminescent clusters in a zeolite A monolayer on quartz [10]. Another great contribution in this regard was the realization of oriented zeolite monolayers with dense packing by introducing covalent bonds between zeolite crystals and the substrate [6,9,11–20]. So far various kinds of covalent molecular linkers have been attached to the surfaces of zeolite and substrates to yield uniformly oriented monolayers of zeolite A, ZSM-5 and zeolite L with high coverage degree and close packing. The attachment of covalent molecular linkers onto the substrates was mainly carried out by reaction between the trialkoxysilyl groups and the OH groups from the substrate surface. Recently, a new type of covalent molecular linker—diisocyanates—has proved to be very effective in preparing oriented zeolite A and ZSM-5 monolayers, thanks to the ready formation of urethane linkages between the isocyanates and the surface hydroxyl groups on substrate and zeolite [21]. Diisocyanates show obvious advantage over silyl compounds in the fabrication of oriented zeolite monolayers because the number of such kind of compounds available is higher than that of silyl compounds [21]. Nevertheless, there has been no report on the preparation of oriented zoelite L monolayer by using DICB as the covalent linker as yet.

We are highly interested in zeolite L monolayers because they can serve as supramolecularly organized light-harvesting systems and as excellent precursors for continuous zeolite films with uniform orientation of the nanopores or nanochannels, which can make the monolayers suitable for application as molecular sieving membranes, nonlinear optical films, and new photonic devices also comprising dye-sensitized solar cells [6,9,30–34]. Consequently, herein we will investigate the preparation of oriented zeolite L monolayers using 1,4-diisocyanatobutane (DICB) as the covalent molecular linker. Another aim of the present work is to elucidate the effect of various covalent molecular linkers on the quality of oriented zeolite L monolayers from the viewpoint of the rigidness of the covalent linkers employed. 1,2-bis(trimethoxysilyl)ethane (BTMSE) with a relative flexible bridging group was used as the covalent molecular linker to fabricate the zeolite L monolayer. The quality of the obtained zoelite L monolayer is compared with those obtained using 1,4-bis(triethoxysilyl)benzene (BTSEB) and 4,4-bis(tiethoxysilyl)biphenyl (BTEBP) as the covalent molecular linker, which have relative rigid bridging groups.

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doi:10.1016/j.jssc.2008.06.023

2. Experimental sections

2.1. Materials

Medium-sized cylindrically shaped zeolite L crystals with 1 μm average length and average aspect ratio (length to diameter ratio) 1.0 were synthesized and characterized as described previously [35,36]. BTMSE, BTSEB and DICB were obtained from Aldrich with high purity.

2.2. Functionalization of quartz with BTMSE, DICB and BTESB

Typically, two pieces of quartz were mounted onto dry toluene solution (10 mL, 0.2 M) of BTME, DIC, and BTESB, respectively, and the solutions were refluxed under dry N_2 for 3 h. After cooling to room temperature, the functionalized quartz were removed from the flask and washed with copious amounts of fresh dry toluene.

2.3. Assembling of zeolite L monolayers on quartz

Dry zeolite L (5 mg) and functionalized quartz were introduced into a round-bottomed flask containing 10 mL of toluene. The mixture was sonicated for 10 min and the zeolite L-coated quartz was removed from the flask followed by sonication for 5 s in fresh toluene to remove physisorbed zeolite L crystals.

2.4. Calcination of zeolite L monolayers

The obtained zeolite L monolayers were placed in an oven with the temperature steadily increased up to 600 °C under oxygen atmosphere.

2.5. Physical measurements

SEM images were carried out by a scanning electron microscope. Sonication of the samples was carried out using an ultrasound-cleaning bath operated at 28 kHz.

3. Results and discussion

One of the most important factors affecting the quality of zeolite L monolayers is the features of zeolite L crystals including the morphology, size distribution and the aspect ratio of zeolite L [32]. It has been shown that only zeolite L crystals with a very flat base, narrow size distribution, and appropriate aspect ratio can be fabricated onto oriented zeolite L monolayers with a high coverage degree and close packing degree. Hence, medium-sized cylindrically shaped zeolite L crystals with 1 μm average length and average aspect ratio (length to diameter ratio) 1.0 having a very flat base as evidenced by the SEM images shown in Figs. 1a and b were used to prepare the oriented zeolite L monolayer. Oriented zeolite L monolayer by using DICB as the covalent molecular linkers was prepared according to the reported procedure as shown in Fig. 2. The quartz remains transparent after treatment with DICB and turns opaque upon contact with zeolite L suspension in dry toluene and vigorous sonication. The opaque quartz became semitransparent after sonication for 10 s in toluene.

Figs. 1c and 1d show the SEM images of the obtained oriented zeolite L monolayer prepared by using DICB as the covalent molecular linker. As evidenced by the SEM images shown in Fig. 1b, the zeolite L crystals display a strong tendency to pack closely during the attachment onto the substrate with a uniform orientation of *c*-axis perpendicular to the substrate and acceptable coverage degree and homogeneity for some applications. This indicates that once zeolite L crystals reacting with the isocyanate group attach to the substrate surface, they tend to act as a template for fixing the next crystals. This also implies that substantial amounts of DICB self-assemble and stand on the substrate surface instead of folding up into a U-shape, which leads to both ends of DICB to react with the quartz surface Thus the free isocyanate group can react with the OH group from zeolite L crystals and direct their arrangement on the quartz [21].

As discussed above, the standing of the covalent molecular linker on the substrate surface should be a prerequisite for obtaining the oriented zeolite monolayer. In order to verify this point, we also prepared an oriented zeolite L monolayer using BTMSE and BTSEB as the covalent molecular linkers. BTSEB is

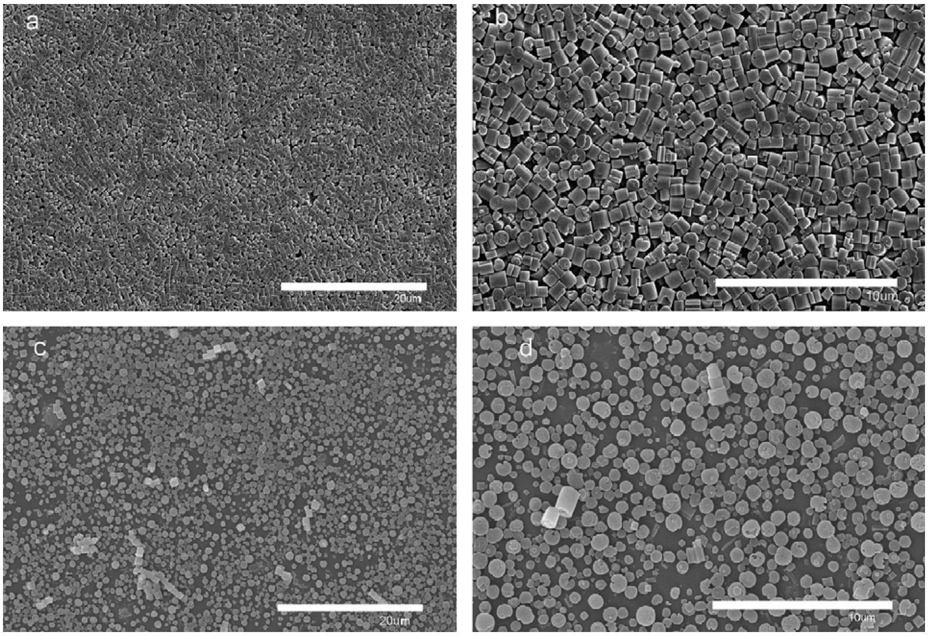

Fig. 1. SEM images of zeolite L crystals (a, b) and the corresponding oriented zeolite L monolayer obtained by using DICB as the covalent molecular linker (c, d).

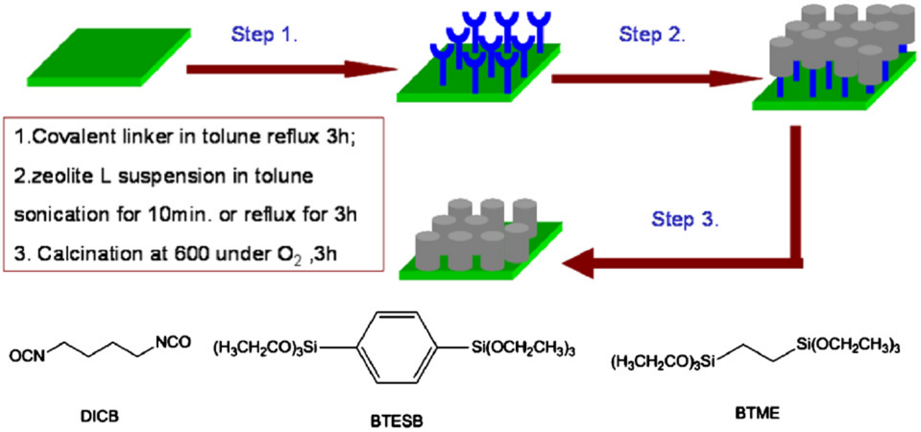

Fig. 2. Procedure for the fabrication of the oriented zeolite L monolayer and covalent molecular linkers used in this study.

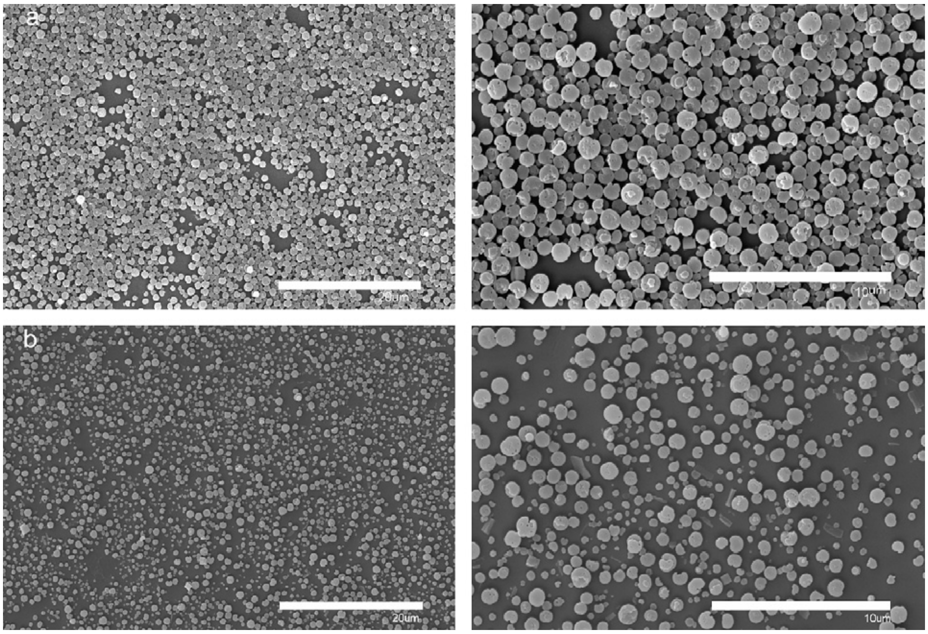

Fig. 3. Oriented zeolite L monolayer prepared by using BTSEB (a) and BTME (b) as the covalent molecular linkers.

a silyl precursor containing a rigid arylene bridging group and has proved to be an effective molecular linker in directing the organization of zoelite L crystals on the substrate surface with the *c*-axis perpendicular to the surface of the substrate. However, BTME is a silyl precursor with a relatively flexible ethane-bridging group. SEM images of the obtained zeolite L monolayers are shown in Fig. 3. As anticipated, the procedure involving BTESB as the covalent molecular linker leads to a very perfect zeolite L monolayer with uniform orientation and dense packing; this is in good agreement with the result published by Gion calzaferri [6]. On the contrary, the use of BTMSE as the covalent molecular linker yielded the zeolite L monolayer, which displays poor packing and coverage on the substrate despite the very uniform orientation. The rigidness of covalent molecular linker we employed could account for the above observation. BTSEB with a rigid bridging group—phenyl ring—tends to be standing on the surface, while BTMSE is very flexible and lie on the substrate surface. Considerable amounts of BTESB stand on the substrate surface due to the presence of the phenyl group, which is very rigid and might self-assemble on the surface via the π–π stacking among the aromatic rings. Thus trialkoxysilyl groups at the end are available for the zeoilte crystals. Both trialkoxysilyl groups in BTME could possibly react with the two OH groups from the glass plate due to the flexibility of the ethane groups; consequently, no or much less trialkoxysilyl groups are available for attachment of zeolite crystals on the surface. This discussion is outlined in Fig. 4. It is worth noting that we also obtained oriented zeolite L monlayers of high quality using BTEBP as the covalent molecular linker, which also has a rigid bridging group [37].

4. Conclusion

Oriented zeolite L monolayers with a good coverage degree and packing degree have been obtained by using DICB as the covalent molecular linker. This research can be helpful in diversifying the type of covalent molecular linker to prepare oriented zeolite L monolayers. The standing of DICB on the substrate surface with

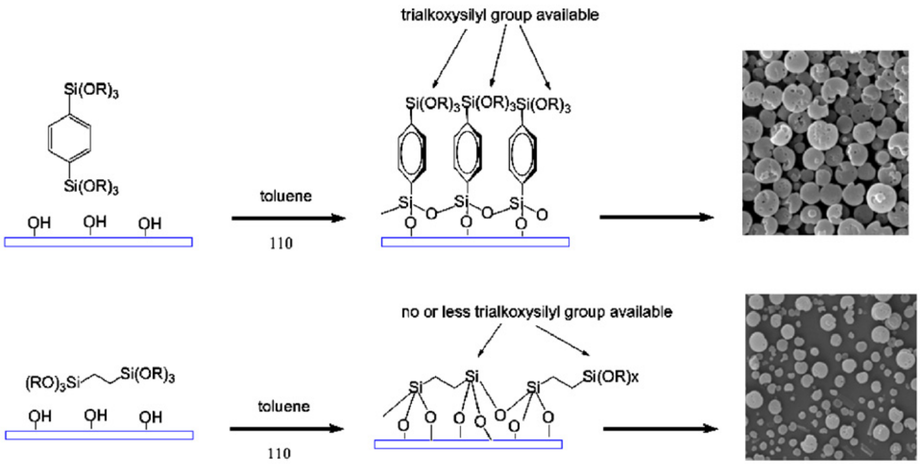

Fig. 4. Proposed model of the covalent molecular linker on the substrate surface.

another isocyanate group available for the attachment of zeolite L crystals has been regarded as the prerequisite for the success in the fabrication of oriented zeolite L monolayers. This can be further demonstrated by the comparison of oriented zeolite L monolayers resulting from BTESB and those prepared by using BTME as the covalent molecular linkers. These new highly organized materials offer unique possibilities of preparing continuous zeolite L thin films with uniform orientation and of developing new photonic devices. The use of the obtained oriented zeolite L monolayer as the precursor to prepare oriented continuous zeolite thin films is under way in our lab.

Acknowledgments

This work was financially supported by Hebei University of Technology, the Key Project of Chinese Ministry of Education (208016), Ministry of Personal, People's Republic of China and Department of Personal, Hebei Province and Scientific program launched in 2008 by Hebei province (08965110D) and National Natural Science Foundation of China (no. 20636030).

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