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SHORT COMMUNICATION

Synthesis of Silicalite-1 Film on a Quartz Superface Using the Vapor Phase Transport Method

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Abstract−Aging and compositional effects of silicalite layer synthesis on a quartz surface using the vapor phase transport method were studied. Silicalite layers can be synthesized from a wide compositional range when not-aged mixtures were used. But reproducibility of the film synthesis was low due to the heterogeneity of the starting mixtures. In order to increase the reproducibility, both aging of the starting mixtures and compositional changes were attempted. Silicalite layer can be synthesized successfully on quartz surface within 0.3 of the ratio $TPAOH/SiO_2$. Higher ratio of $TPAOH/SiO_2$ smaller crystals are formed. If the $TPAOH/SiO_2$ ratio is larger than 0.3, the formed silicalite crystal cannot be attached on the quartz surface. When the $TPAOH/SiO_2$ ratio of the aged starting mixture was 0.28, requirements for both reproducibility and smaller crystal size resulted were satisfied. The crystal size and shape in the silicalite layer are also influenced by the water content in the mixture. The crystal size in the silicalite layer increases with increasing water content in the mixture.

Key words: Silicalite Film, Quartz Surface, Aging Effect, Compositional Effect

INTRODUCTION

Zeolites are finding widespread application in all fields of molecular recognition phenomena. No longer are they just of interest in the area of catalytic, ion-exchange and separation science. Because they have uniform porous structures and ion-exchange capacity, zeolites have been endowed with selectivities in molecular shape and adsorption. Therefore, the applications for new materials such as zeolite film and membranes are very promising [Matuskata et al., 1992; Bai et al., 1995; Liu et al., 1996]

Zeolites are generally microcrystalline materials with typical crystal sizes in the range 0.1-200 μm. Zeolite coatings have many applications to catalysis, membrane separation and sensing molecules. Great interest has been focused on the synthesis of zeolite membranes and films because of their uniform pore sizes, and thermal and chemical resistance. In recent years zeolite membranes have been prepared by in situ synthesis on porous supports, and these membranes were able to separate mixtures by utilizing molecular sieving and selective adsorption of the zeolite pores [Coronas et al., 1997].

Zeolite films also could impart shape-selective properties to ceramic materials. The surface areas of chemical sensors such as surface acoustic wave devices as shown in Fig. 1 [Bein et al., 1989; Plog et al., 1995] and semiconductor gas sensors [Moseley, 1992] could be increased by embedding zeolite films. In addition, the adsorption properties of zeolite films could be controlled by adjusting the composition of the zeolites and/or by ion change.

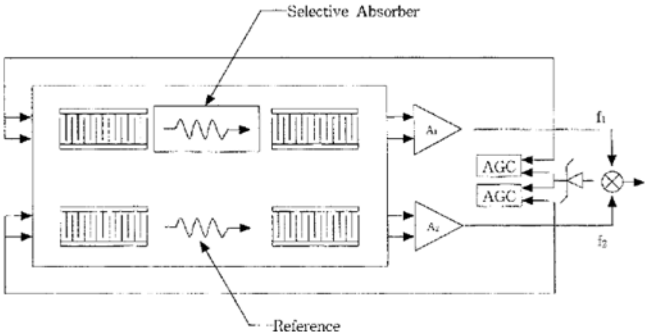

Fig. 1. Dual delay-time configuration in the SAW device.

Zeolite coatings on supports can be synthesized by in situ synthesis [Yan et al., 1995] or by applying a zeolite phase synthesized [Sterte et al., 1997]. In this work, synthesis of silicalite crystal layers on quartz surface using the vapor phase transport method was studied. In comparison with the conventional hydrothermal synthesis method, the vapor phase transport method can cut down both the amount of chemicals spent and pollution problems. As liquid, sols or mixtures of specific compositions can be transformed into silicalite structure in autogenous vapor pressure at 150 °C [Jung et al., 1998]. In addition, a silicalite layer on the quartz surface can be synthesized by utilizing this method. Aging and compositional effects of the starting mixtures on the synthesis of silicalite crystal layers were studied. With a view to increasing the reproducibility of the silicalite film synthesis, fully aged homogeneous mixtures were employed and tested as starting source materials. Both optimum conditions and composition for the synthesis of silicalite layer were sought in order to increase reproducibility in the synthesis.

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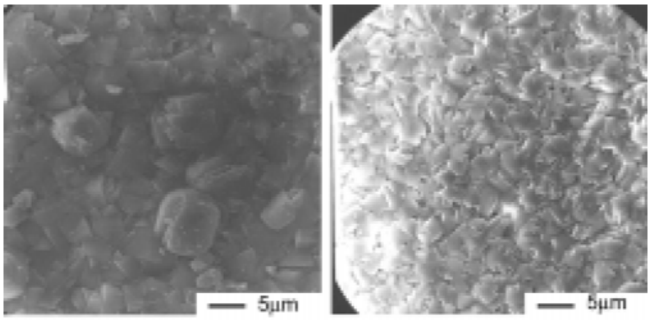
EXPERIMENTAL

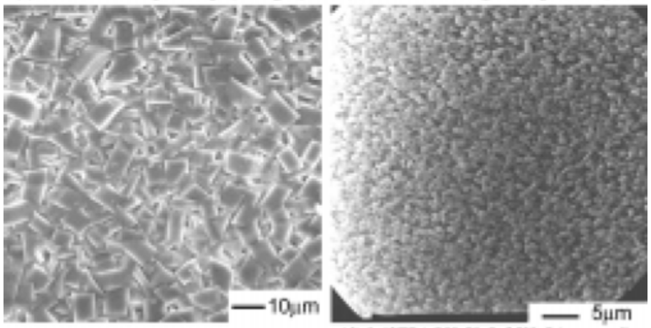
Single crystals of quartz plates (its diameter and thickness were 2.54 cm and 1 mm, respectively) were employed as support materials. Tetrapropylammoniumhydroxide (TPAOH 40 wt% Johnson Matthey Electronics, and 20 wt% Aldrich), Ludox AS-40 and Tetraethylorthosilicate (TEOS) (Aldrich Chemical Company Inc.) were used as source materials for the synthesis of the silicalite layer. With a view of coating silicalite film on the specific area of the quartz surface, an organic polymer material (AC-828, Adcoat CO.) was employed as a masking substance.

Not-aged starting source materials were added on the specific area (0.25 cm^2) for the synthesis in sequence as follows: a few drops (one or two drops) of aqueous TPAOH solution was put on the specific area, and then a few drops of aqueous silica solution was added to the previous TPAOH solution with a micropipette.

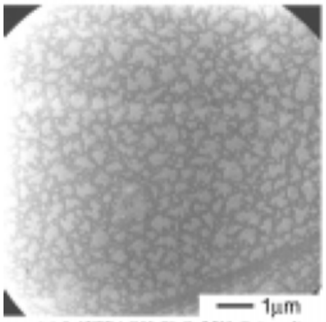
Aged mixtures were prepared by overnight stirring with a rotating magnetic bar in a bottle made of polyethylene. A drop of starting mixture was put on the specific area of the plates. Distilled water (5 g) was also put on the bottom of the Teflon vessel. The volume of the Teflon vessel occupied by liquid and gas was 40 ml. A pressure vessel containing the quartz plate, as shown in Fig. 2, was sealed and kept in the air heated oven at 150 °C for one day. A hydrothermal equilibrium state is established between the mixture and water vapor with heating. Silicalite was formed in this hydrothermal state. After synthesis, the bomb was cooled down by air. The resulting silicalite layer attached to the quartz surface was washed with distilled water, and calcined at 823 K for 5 hours. The silicalite layers were then investigated with XRD analysis and scanning electron microscopy (SEM).



(a) 0.14TPAOH-Si_2O-11H_2O(not-aged) (b) 0.24TPAOH-Si_2O-25H_2O(not-aged)



(c) 0.28TPAOH-SiO_2-20H_2O(aged) (d) 0.43TPAOH-Si_2O-25H_2O(not-aged)



(e) 0.43TPAOH-Si_2O-25H_2O (aged)

Fig. 3. SEM of the surface of the silicalite layers synthesized with different compositions.

RESULTS AND DISCUSSION

To observe the compositional effect on the synthesis, three starting compositions were prepared and those mole ratios were as follows: (a) 0.14TPAOH-SiO_2-11H_2O, (b) 0.24TPAOH-SiO_2-25H_2O, (c) 0.28TPAOH-SiO_2-20H_2O and (d) 0.43TPAOH-SiO_2-25H_2O. Silicalite crystal layers were formed on the quartz surface as shown in Fig. 3. When the starting mixtures were not aged, silicalite layers were successfully synthesized from the wide composition range. A lump of amorphous silicate phase was also found over the silicalite layer when the pressure vessel was cooled down and opened. The silicalite layer was covered with an amorphous phase. A few silicalite crystals were sparsely positioned in the amorphous phase. Both the amorphous silica phases and the silicalite crystals located in the amorphous phases were easily removed by washing. The size of the silicalite formed was decreased with increasing TPAOH content in starting materials. In low TPAOH content a large size of silicalite resulted and intergrowth between crystals was good as shown in Fig. 3(a), (b) and (c). In case of high TPAOH content small silicalite was obtained and intergrowth was poor. The existence of cations is known as essential in most zeolite syntheses. Without cation sources (Na^+, TPA^+), no ZSM-5 crystals can be formed. Cations are believed to function as structure-directing agencies or nuclei sites from the relations with anions such as silicates or aluminosilicates. The sites such as Na^+ and TPA^+

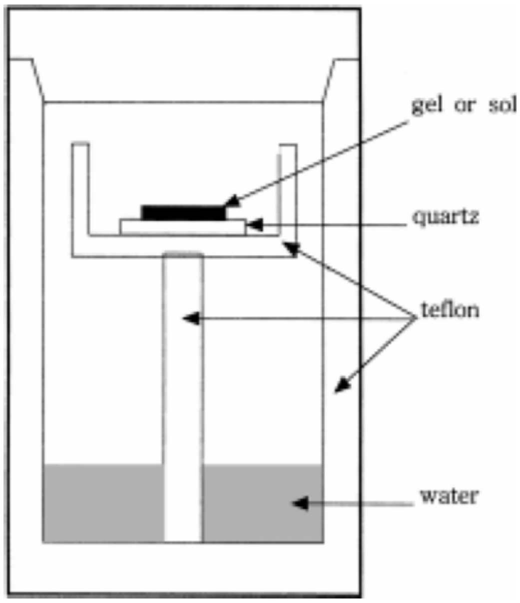


Fig. 2. Experimental arragement for the synthesis of silicalite-1.

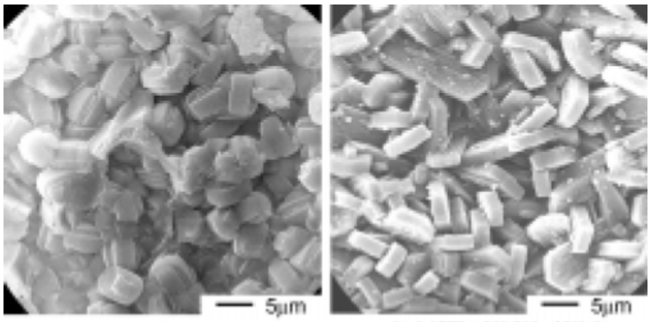
enclosed with silicate anions are believed to be active sites for nucleation. Also, these cation sites are also regarded as starting points of crystallization [Jung et al., 1998]. It can be deduced that the number of nuclei is increased with increasing content of TPAOH; therefore, crystal size is decreased, and intergrowth between crystals is also decreased.

Aged starting mixtures having the same content were also employed to evaluate the aging effect. In the cases where the aged mixtures (a) and (b) were used, the same results as the one from the not-aged were obtained as shown in Fig. 3(a) and (b), respectively. Both crystal layers and shapes obtained from the aged were the same with those from the not-aged mixtures. However, no silicalite crystal stuck on the surface was found when the aged mixture (d) was used as shown in Fig. 3(e). A powder form of silicalite was synthesized only. We know that the aging effect is less important at lower TPAOH concentration than at higher TPAOH concentration.

When the not-aged mixtures are used, silicalite layers can be synthesized in the wider composition range. However, reproducibility in the film synthesis was low due to the heterogeneity of the starting mixtures. Reproducibility is an important factor in application for industrial processes and quality control. The reproducibility can be improved by employing a homogeneous aged-mixture. The not-aged mixture was changed into a single aged phase by continuous stirring. Thus, the not-aged mixtures were stirred for 12 hours for the synthesis.

When the TPAOH/SiO_2 ratio of the aged mixture was over 0.40, no silicalite layer was formed, but powdery crystals resulted. Larger crystal size resulted when a smaller TPAOH/SiO_2 ratio was used. Smaller crystal is better for obtaining quick responses in applications for chemical sensors. Therefore, the optimum condition for the synthesis of smaller crystal attached on the surface was searched with the aged mixtures. When the aged mixture of 0.28TPAOH-SiO_2-$20H_2O$ (aged) was used, relatively smaller crystal was successfully formed on the quartz plate as shown in Fig. 3(c). The XRD patterns of silicalite-1 formed on the surface layer are shown in Fig. 4.

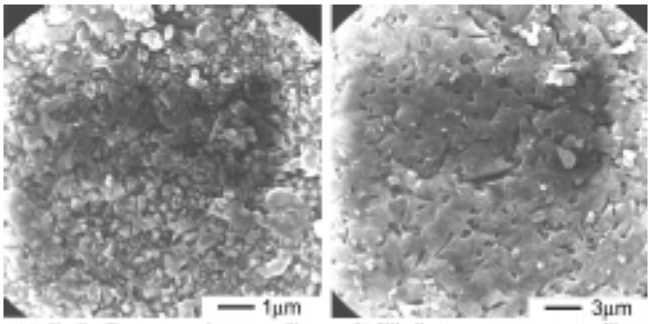
The crystal size and shape in the silicalite layer is also influenced by water content in the mixture. The crystal shape in the silicalite layer becomes thinner and larger with increasing water content as shown in Fig. 5. With increasing content of water, the mobility of silicate anions increased; as a result, silicate anion is easier to find out the optimum points to be assembled. Thus, the crystallinity of the sample in Fig. 5(b) is higher than that of the sample in Fig. 5(a).



(a) 0.07TPAOH-SiO_2-$6H_2O$ (b) 0.07TPAOH-SiO_2-$33H_2O$

Fig. 5. SEM images of silicalite layers obtained from different water compositions.

When the excess silica source (AS-40) was added to the quartz surface slightly wetted with TPAOH solution, the silicalite crystals grew within the excess amorphous silica phase as shown in Fig. 6(a). It is considered that the silicalite crystals started to grow up from the nuclei at the quartz surface to the upper direction. A small portion of TPAOH was mixed with the excess silica by convection flow; thus, a few silicalites grew in the silica phase as



(a) silicalite film grown under excess silica (b) Silicalites grown among excess silica

Fig. 6. Silicalite crystals and film grown in excess silica phase.

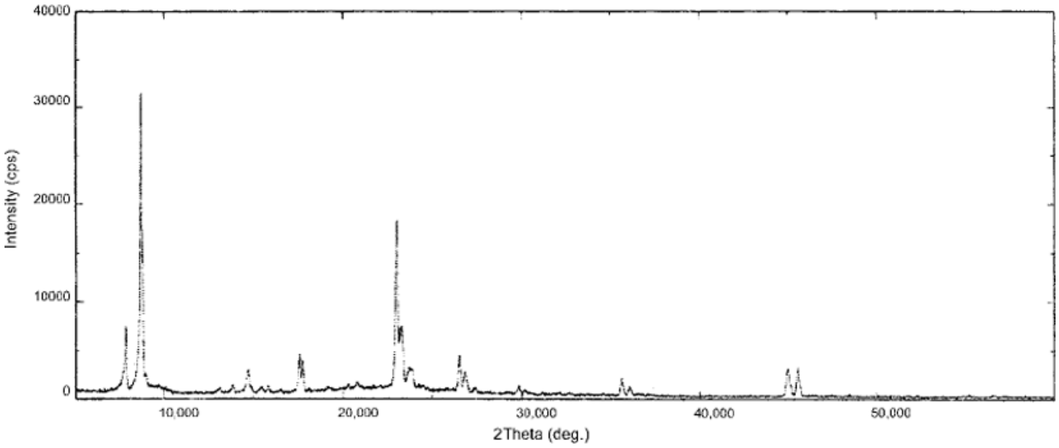


Fig. 4. The XRD patterns of silicalite-1 grown on the quartz surface.

shown in Fig. 6(b). Also, amorphous silica around silicalites was transferred to the silicalite surfaces through the condensed aqueous phase, and then transformed into the silicalite structure.

CONCLUSIONS

The vapor phase transport method for the synthesis of silicalite layer can cut down the amount of chemicals used and reduce pollution problems. Employing the not-aged mixtures for the synthesis of the silicalite layer enlarged the composition range of the starting mixture. However, the reproducibility of the silicalite film synthesis was low due to the heterogeneity of starting mixtures when the not-aged mixtures were used. In order to increase the reproducibility in the synthesis of small silicalite layer, an optimum content of aged mixture was searched for. When the TPAOH /SiO_2 ratio of the aged mixture was over 0.40, no silicalite layer was formed, but powdery crystals resulted. Larger crystal size resulted when a smaller TPAOH/SiO_2 ratio was used. At lower TPAOH content, crystal sizes were larger and intergrowth between crystals was better. The size of silicalite formed on the quartz surface decreased with increasing TPAOH content in starting mixtures. Smaller crystal is better for obtaining quick responses in applications for chemical sensors. At higher TPAOH content (TPAOH /SiO_2 ratio<0.4), smaller silicalite resulted and intergrowth between crystals was lower. Therefore, the optimum condition for the synthesis of smaller crystal attached on the surface was the aged mixture of 0.28TPAOH-SiO_2-20H_2O (aged) as shown in Fig. 3(d).

The crystal size and shape of the silicalite layer are also influenced by water content in mixture. The crystal shape in the silicalite layer became thinner and larger with increasing water content due to the increased mobility of silicate anions. Silicalite crystals started to grow up from the nuclei on the quartz surface wetted with TPAOH solution. However, a small portion of TPAOH was mixed with the excess silica by convection flow; thus, a few silicalites grew in the amorphous silica phase. Also, amorphous silica around silicalites was transferred to the silicalite surfaces through the condensed aqueous phase, and then transformed into the silicalite structure.

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