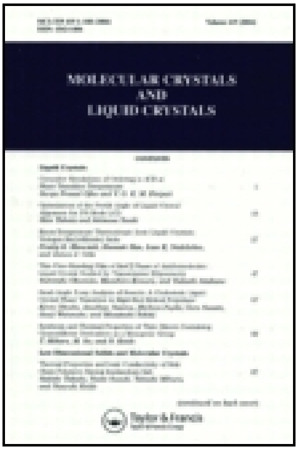

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Influence of solid-state transformation time on the nucleation and growth of silicalite 1 prepared from layered silicate

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Influence of solid-state transformation time on the nucleation and growth of silicalite 1 prepared from layered silicate

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The nucleation and crystals growth of silicalite 1 precursors synthesized by solid state transformation was studied using X-ray diffraction, thermal analysis, infrared spectroscopy, ^{29}Si and ^{13}C NMR and electron microscopy. Silicalite 1 was obtained after 16 hours at 130°C in closed glass ampoule. The comparison with hydrothermal synthesis showed that the characterization of the precursors presents some similarities, however, nucleation and crystals growth were much shorter for solid state transformation. ^{29}Si NMR showed that nucleation started during the first stage (cation exchange) for solid state transformation, but only during the second stage for hydrothermal synthesis. It was also observed that the major changes occur during the beginning of crystals growth for solid state transformation but during nucleation for hydrothermal synthesis. The results were explained by the fact that the starting materials were completely different : single layered silicate for solid state transformation and colloidal silica for hydrothermal synthesis.

Keywords : silicalite, template, solid state transformation, layered silicate

INTRODUCTION

Recently, the synthesis of silicalite 1 has become more and more important because of its good gas and liquid separation behaviour[1]. Silicalite 1 can be synthesized by hydrothermal method in autoclave after 10 days at 110°C[2]. However, to shape silicalite into disk with this method, it is necessary to use binders which decreases the crystallinity of the material. A new solid state transformation method which enables to make silicalite disks without using binders has been reported by Shimizu *et al.*[3]. They have prepared silicalite disks from single layered silicate (kanemite) and short-chained alkylammonium cation after 46 hours of thermal treatment at 130°C. They have also observed by SEM that silicalite crystals were smaller and more uniform than the ones obtained through hydrothermal synthesis.

In this present work, we will characterize the products from solid state transformation as a function of time in order to obtain a better understanding of the nucleation and crystallization process. A comparison will be done with hydrothermal synthesis.

EXPERIMENTAL

Silicalite 1 was synthesized by dispersing kanemite into a tetrapropylammonium hydroxide (TPAOH) solution. The pH was adjusted to 11 and the mixture was stirred at 70°C for 3 hours. During that stage, cation exchange $Na^+ \rightarrow TPA^+$ occurred. After cooling down to room temperature, the pH was adjusted to 8.5, at that time, a gel was obtained. After filtration and drying, the intercalated kanemite powder was shaped into disk. The disk was introduced in a glass ampoule which was closed and put in an oven at 130°C. Sample were periodically withdrawn and analyzed by X-ray diffraction, thermal analysis, infrared spectroscopy, ^{29}Si and ^{13}C NMR and electron microscopy.

RESULTS AND DISCUSSION

Figure 1 summarizes the main results which were obtained. ^{29}Si NMR had showed that Q_3/Q_4 ratio decreases during both cation exchange and solid state transformation, indicating that nucleation process starts during cation exchange. X-ray diffraction patterns showed that crystals growth started after 1h 50 mn of solid state transformation. From XRD, thermal analysis and SEM, it was concluded that a material presenting the characteristics of silicalite 1 was obtained after 16 hours of solid state transformation. Thermal analysis showed that dehydration phenomenon occurs during crystallization time, corresponding to the cross-linking of kanemite layers, that is the building of the 3 dimensional network. The increase in XRD and IR crystallinities and decrease in TPA decomposition temperature after 46 hours of solid state transformation were explained by the appearance of crystalline fibers of silicalite 1.

As for the comparison with hydrothermal synthesis[2, 4, 5], the starting materials and the experimental conditions are summarized in Table I. As can be seen, the starting materials are completely different : crystalline layered structure silicate powder for solid state transformation and amorphous silica powder for hydrothermal synthesis. The products obtained after the first stage are also different : intercalated silicate powder in the first case and colloidal silica gel in the second case.

Despite the different starting materials and experimental conditions, the characterization of the products obtained by both kinds of synthesis presents some similarities. As a matter of fact, increase of the 550 cm^{-1} absorption band, dehydration phenomenon, increase of TPA$^+$ decomposition temperature, decrease in Q_3/Q_4 ratio and splitting of the methyl group resonance of the template were also observed for hydrothermal synthesis. 3 to 4 TPA$^+$ were present per unit cell and the interactions between the template and the framework were strong (IR, NMR). However, although a sigmoid nucleation-growth crystallization kinetics characterizes both types of synthesis, the induction period (nucleation) and the crystallization period

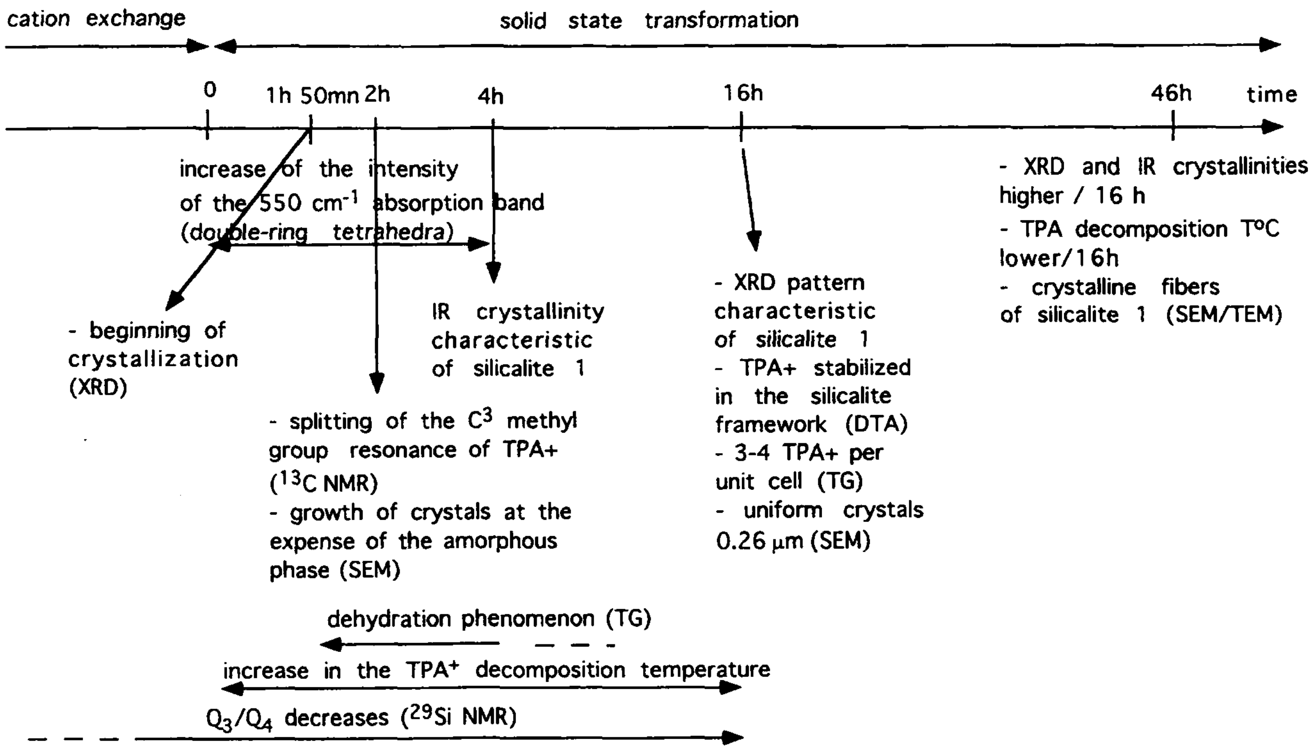


FIGURE 1 Characterization of silicalite 1, summary of the results

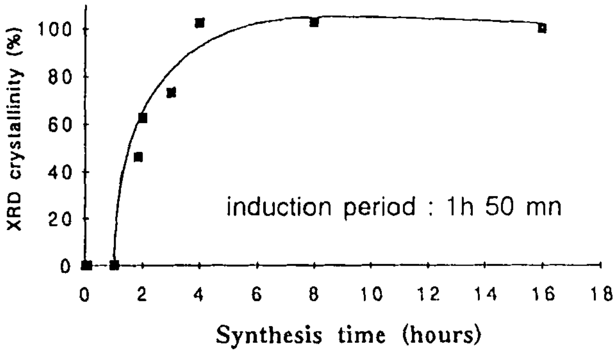
TABLE I Starting materials and experimental conditions of solid state transformation and hydrothermal synthesis

Solid state transformation	**Hydrothermal synthesis**
Starting materials	
layered structure silicate powder (crystalline)	SiO_2 powder (amorphous)
TPAOH solution	TPABr or TPAOH solution
Experimental conditions	
- pH adjusted to 11	- pH adjusted to 10-11
- stirring at 70°C, 3 h : cation exchange	- stirring at room temperature, 3 h for Silicalite 1
	- aging at 25°C overnight for ZSM-5
- pH adjusted to 8.5 ⇨ gel	
- filtration, drying	
⇨ intercalated silicate powder	⇨ polymeric silica gel for silicate 1
	⇨ aluminosilica gel for ZSM-5
- solid state transformation in closed glass ampoule	- hydrothermal treatment in autoclave

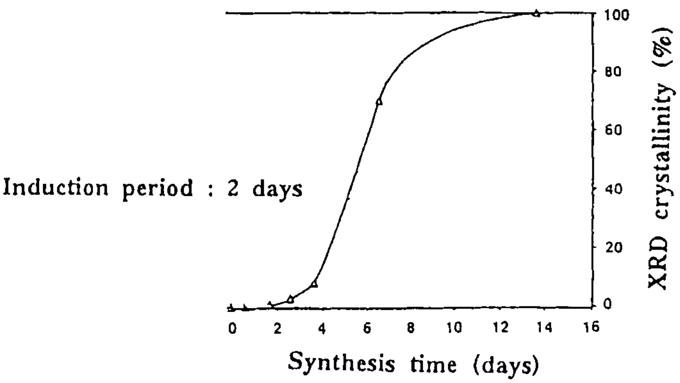
(crystals growth) were much shorter for solid state transformation (figure 2). ^{29}Si NMR also showed that nucleation (increase of Q_3/Q_4 ratio) started during the first stage (cation exchange) for solid state transformation, but only during the second stage for solid state transformation. It was also observed that the greatest variations in Q_3/Q_4 ratio occur during the beginning of crystallization for solid state transformation but only during nucleation for hydrothermal synthesis (figure 3). The results were explained by the fact that the starting materials were completely different. As a matter of fact, the silicalite network can be built much more rapidly if the starting material has a 2 dimensional structure beforehand.

CONCLUSION

The study of the influence of solid-state transformation time on nucleation and crystals growth of silicalite 1 prepared from layered silicate has showed that the microporous material could be obtained after 16 hours at 130°C. From the comparison with hydrothermal synthesis, it was noticed that

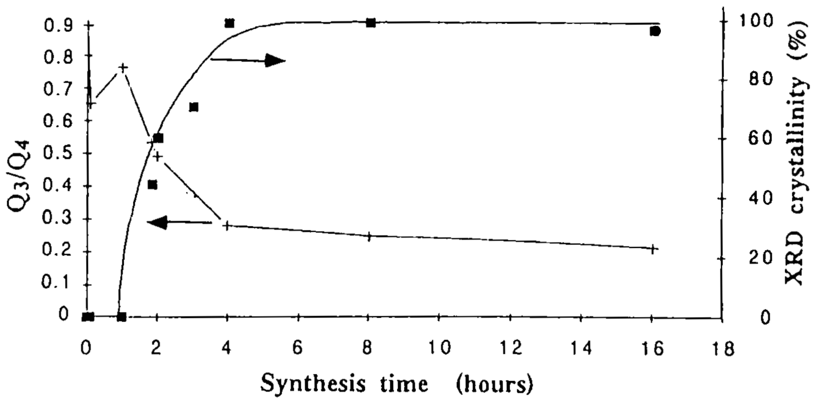


Solid state transformation of silicalite 1

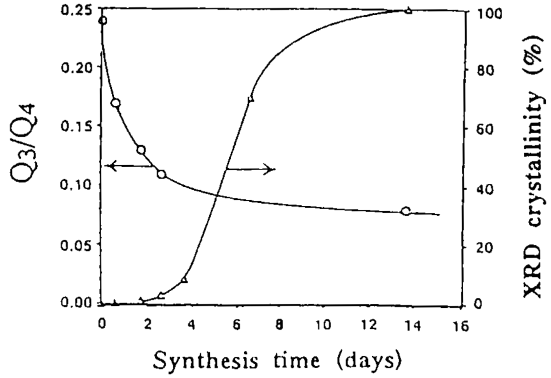


Hydrothermal synthesis of zeolite ZSM-5

FIGURE 2 Change of XRD crystallinity with synthesis time



Solid state transformation of silicalite 1



Hydrothermal synthesis of zeolite ZSM-5

FIGURE 3 Change of XRD crystallinity and Q_3/Q_4 ratio with synthesis time nucleation and crystals growth were much shorter for solid state transformation. It was also observed that the major changes occurred during the beginning of crystals growth for solid state transformation and during nucleation for hydrothermal synthesis. The results were explained by the fact that the starting materials were completely different. As for solid state transformation, the layered structure material built beforehand enables nucleation to start during cation exchange and shortens drastically the synthesis time.

Acknowledgements

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