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Gelation Behavior of Three-functional Silanes for Preparation of Mesoporous Silicas (I)

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We studied on the gelation behavior in a sol-gel reaction of three-functional silanes under various reaction parameters such as solvents, concentration of catalyst, and gelation time. Trimethoxyvinylsilane(TMVS) or Triethoxyvinylsilane(TEVS) was used as a precursor and poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide)(EPE) was used as a structure directing agent.

Keywords: gelation behavior; three-functional silane; template.

INTRODUCTION

The discovery of ordered mesoporous materials opened new and rapidly growing field of modern science and technology, expanding the range of periodic porous materials into the mesoporous region^[1] Hybrid mesoporous sieves take advantage of the properties of the inorganic support, as well as of the organic surface groups. Various methods have been reported that functionalize the surface of periodic mesoporous materials containing organic groups because surface modification permits tailoring of the surface properties for numerous potential application^[2,3].

We studied on the gelation behavior in a sol-gel reaction of three-functional silanes under various reaction parameters such as solvents, concentration of catalyst, and gelation time. In general it is well known that gelation time is one of the controlling factors to prepare porous

materials having a nanometer size, when prepared by sol-gel reaction. In addition, the shapes of materials were changed as a function of gelation time. In this work, we investigated the factors influencing gelation time and the shapes of three-functional silanes, especially concentration of solvent and catalyst^[4,5].

EXPERIMENTAL

Materials. Trimethoxyvinylsilane(TMVS, 98%), triethoxyvinylsilane (TEVS, 97%), poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide (EPE, 5800), polyethylene glycol(PEG, 3400) were purchased from Aldrich. Methanol(99%), ethanol(95%) and sodium hydroxide(96%) was from Duksan Chemical Company, Korea.

Synthesis. First, EPE was mixed with a solvent containing methanol or ethanol and base catalyst(sodium hydroxide) and stirred for 40 minutes at 40°C. PEG was added to this solution and further stirred for 60 minutes. Then, TMVS or TEVS was put into this solution and stirred for 120 minutes. The product was filtered, washed by neutral aqueous solution, and dried in air at ambient temperature. As-synthesized samples was calcined at 500 °C for 6h.

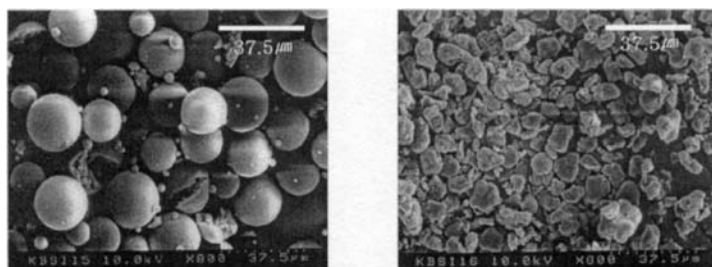
Analysis. X-ray powder diffraction patterns were measured on 4C2(SAXS) of beam lines in Pohang Accelerator Laboratory, POSTECH, Korea. Scanning Electron Micrographs(SEM) were performed on HITACHI S-4200.

RESULTS AND DISCUSSION

The control of gelation time is very important for controlling the shape of materials, because organo-functional silane has high reactivity compared with tetraethoxysilane(TEOS) or tetrametyoxysilane (TMOS).^[6] Table 1 shows the effects of solvents and catalyst on the gelation time and precipitation. When the concentration of catalyst is constant, gelation time is increased with increasing the concentration of methanol. The gelation time reaches to more than 10hrs at high concentration (80wt%) of methanol. On the contrary, when the concentration of solvent was constant, gelation time was decreased with increasing the concentration of catalyst. Fig.1 shows representative SEM micrographs of as-synthesized samples. Most of powders are likely to form sphere

Table 1. The effects of solvents and catalyst on the gelation time and precipitation

Symbol	Source	MeOH (wt%)	EtOH (wt%)	NaOH (mol)	Gel time	Precipitation
MVM-0	TMVS	0	–	0.0133	$\leq 5''$	Wet gel
MVM-1	TMVS	10	–	0.0133	1' 50''	Powder
MVM-4	TMVS	40	–	0.0133	4' 50''	Powder
MVM-8	TMVS	80	–	0.0133	$\geq 10\text{h}$	Glass
MVS-2	TMVS	40	–	0.0062	4' 50''	Powder
MVS-5	TMVS	40	–	0.0133	1' 37''	Powder
MVS-8	TMVS	40	–	0.0219	33''	Powder
MVE-1	TMVS	–	10	0.0133	1' 20''	Powder
MVE-4	TMVS	–	40	0.0133	4' 30''	Powder
EVE-1	TEVS	–	10	0.0133	$\leq 5''$	Wet gel
EVE-4	TEVS	–	40	0.0133	$\leq 5''$	Wet gel



(a)

(b)

FIGURE 1 Scanning electron micrographs(SEM) of as-synthesized samples. (a) MVE-4 (b) MVM-8

shape and glass or wet gel tends to make plate shape. In case of TMVS, when the concentration of catalyst was constant, powder was preferred to form at low and medium concentration of solvents and glass was formed at high ones. When ethanol was used as a solvent, if the concentration of catalyst was constant and the concentration of ethanol was changed, powder was formed at low concentration and glass was formed at medium and high concentration as well. In case of TEVS, however, on changing the concentration of ethanol, wet gel was formed at low and medium concentration and glass was formed at high concentration. Morphology of as-synthesized samples are greatly influenced by the concentration of solvent but not very affected by the

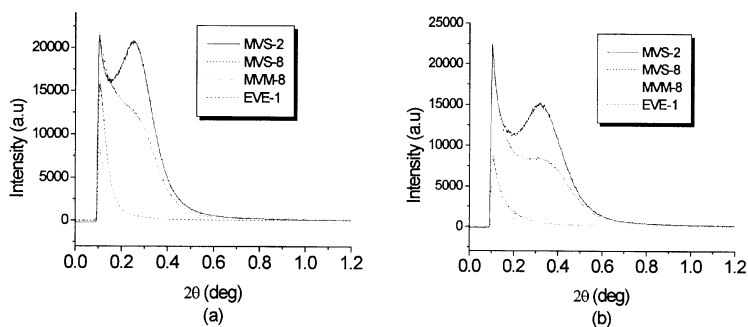


FIGURE 2 Small angle X-ray scattering(SAXS) patterns of as-synthesized (a) and calcined (b) samples under different experimental conditions

concentration of catalyst. It should be noted that from Table 1 that by controlling gelation time, powder shape of precipitation products could be obtained. If gelation time was too short or long, glass or wet gel would be formed. Figure 2 shows SAXS patterns of as-synthesized and calcined samples. Wet gel and glass type of samples displayed amorphous silica behaviors and powder samples were likely to show short-range periodic structure. The intensity was increased due to removal of surfactant and organic moiety of three-functional silanes after calcinations. We confirmed that the morphology of materials affected on the short-range periodic structure from the SAXS patterns. Therefore, it may be concluded that the periodic structure of three-functional silanes can be formed by controlling morphology of materials, which is influenced by gelation time, concentration of solvents and catalyst.

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Reference

- [1] M.Jaroniec, R.Ryoo, J.M.Kim, *Chem. Mater.*, **11**, 2568 (1999)
- [2] M.K.Lim, A.Stein, *Chem. Mater.*, **11**, 3285 (1999)
- [3] F.J.Feher, D.A.Newman, *J. Am. Chem. Soc.*, **112**, 1931 (1990)
- [4] A.Corma, *Chem. Rev.*, **97**, 2373 (1997)
- [5] L.L.Hench, J.K. West, *Chem. Rev.*, **90**, 33 (1990)
- [6] Y. Dubitsky, G.Zannoni, L.Zetta, *Mater. Chem. & Phys.*, **64**, 45 (2000)