Evaporation-induced Self-assembly for Meso-porous Materials Studied by X-ray Diffraction

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Lately we found that the SnO_2 crystallites in nanorod shape homogeneously embedded into the meso-channels of large mesoporous silica materials could be synthesized in an one-step process, including aqueous sol-gel and hydrothermal synthesis approach when the Sn/Si molar ratios in the gel was in the range of 0.05- 0.1. The phase transformation from 2D hexagonal *P6mm* to 3D hexagonal $P6_3mmc$ pore structure was observed by using *ex-situ* XRD technique. The size of crystallized SnO_2 nanorods with tetragonal phase was 5 – 10 in diameter and 10 – 30 nm in length. The SnO_2 nanorods were composed of small SnO_2 nanoparticles with size of 5 nm in diameter and they were mainly located inside the meso-channels, confirmed by using HRTEM technique.

The formation of pore structure of gelled 0.1Sn-MSM sample during the reaction period was surveyed by an *in-situ* XRD technique at beam line 17A of NSRRC and the result is shown in Figure 1. The 2D-hexagonal *P6mm* pore structure was found when the reaction was carried out for 1 h. The structural ordering of 2D-hexagonal was enhanced by increasing the reaction period. Interestingly, the phase transition from 2D-hexagonal *P6mm* to 3D-hexagonal $P6_3mmc$ was observed after the synthesis solution was reacted more than 11 h. Further increasing the reaction time, no phase transformation was found. It revealed that the stable mesostructure of $0.1SnO_2$-MSM sample in the gel condition was 3D-hexagonal $P6_3mmc$ pore structure. The phase transition seemed to be dependent on the Sn/Si ratio in the gel. The relationship between phase transition and Sn/Si ratio will be investigated in detail in the future work.

The *in-situ* XRD pattern of $0.1SnO_2$-MSM sample in the period of hydrothermal treatment is displayed in Figure 2. The three well-resolved diffraction peaks in low angle region changed into a relatively narrowed peak at 2 $\theta = 0.58^o$ with a shoulder at 2 = 0.63^o which corresponded to the results of 131.7 and 121.2 Å in spacings, respectively. It demonstrated that the structural shrinkage and re-organization of pore wall occurred during the hydrothermal treatment. Finally, the shape and position of diffraction peaks of $0.1SnO_2$-MSM sample hydrothermally treated for 1.5 h was similar to the solid product measured by an *ex-situ* XRD. The pore structure was still look like a 3D-hexagonal pore arrangement. However, it was not easy to identify the mesostructure based on the broad diffraction peaks in the low angle position. The further investigation of thermal treatment on the mesostructured shrinkage and re-construction is needed.

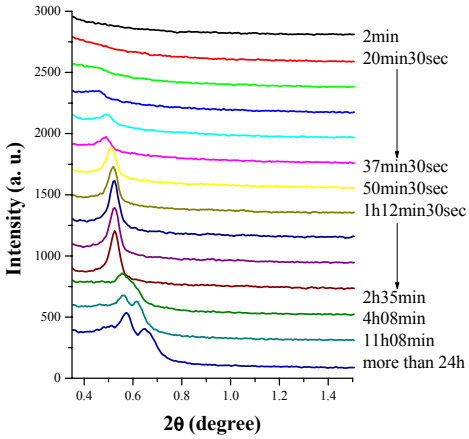

Figure 1. The *in-situ* XRD patterna of gelled $0.1SnO_2$-MSM in the reaction period.

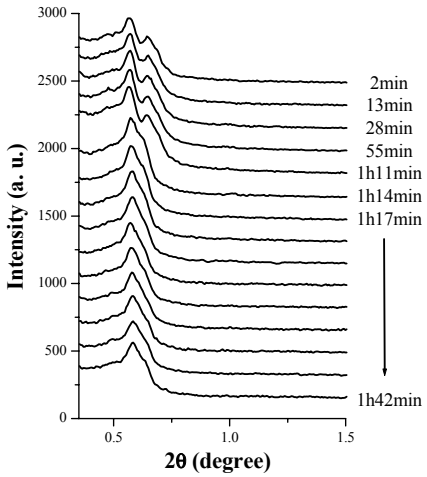

Figure 2. Effect of hydrothermal treatment on the mesostructure of gelled $0.1SnO_2$-MSM.