

***In-Situ* XRD Studies on the Self-Assembly Process of Organic Functionalized SBA-15 Mesoporous Materials with Platelet Shape and Short Mesochannels**

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Molecular diffusion through the mesochannels and pore blockage along the channeling pores of SBA-15 with the diameters varied in 2-10 nm and lengths in a scale of micrometer, are the main concern when applying these materials for sorption and catalysis. Here, we report a facile synthesis route for preparing SBA-15 silica of platelet shape and very short mesochannels (150–350 nm). Moreover, the synthesis route can be easily extended to prepare SBA-15 materials with various organic functional groups up to 1.87 mmol/g loading in one pot. We have studied the self-assembly processes by the *in-situ* XRD technique at beam line 17A of NSRRC, Taiwan, and reported here.

The compositions of SBA-15 gels prepared with Zr(IV) ions were 0.017 P123 : 1.0 TEOS : 0–0.1 ZrOCl₂ : 7.94 HCl : 221 H₂O. For the SBA-15 prepared with a Zr/Si ratio of 0.05, a diffraction peak at $2\theta = 0.61^\circ$ ($d = 14.5$ nm) was promptly seen after adding TEOS for 7.3 min (Fig. 1(a)). The white solid was also seen at this moment. The (110) and (200) diffraction peaks appeared after about 30 min. Fig. 1(b) shows the effect of Zr/Si ratio on the time needed for the first appearance of diffraction peak (designated as τ). It was found that the τ value decreases gradually and lowers from ca. 52 to 7 min when 12.5 mM of ZrOCl₂ was added. These results demonstrate that the formation of ordered mesoporous silica is accelerated by Zr(IV) ions.

Pre-hydrolysis of TEOS is essential step to obtain well-ordered SBA-15 materials with high loading of organic functionality in one pot. The 10 mol% of CH₃-functionalized SBA-15 with platelet morphology and short mesochannels was prepared with TEOS prehydrolysis for 1. Fig. 1(c) shows that a broad diffraction at $2\theta \sim 0.61^\circ$ was observed in several minutes in the acidic solution with containing TEOS, P123 and Zr(IV). The peak grew stronger and sharper as the reaction progressed. When (CH₃O)₃SiCH₃ (MTES) was added into the synthesis gel after 1 h, the diffraction peak immediately weakened and moved toward higher-angle. Nevertheless, the diffraction peak regained its intensity in the next 5 min and grew gradually without moving the position significantly. After TEOS was added for 1.5 h, the (110) and (200) diffraction peaks appeared at $2\theta \sim 1.13$ and 1.28° . These results indicate that the self-assembly of P123 micelles and TEOS is slightly perturbed by MTES, but adding Zr(IV) species in the synthesis solution still dominates the rate of mesoporous silica formation which induce formation of SBA-15 with short mesochannels.

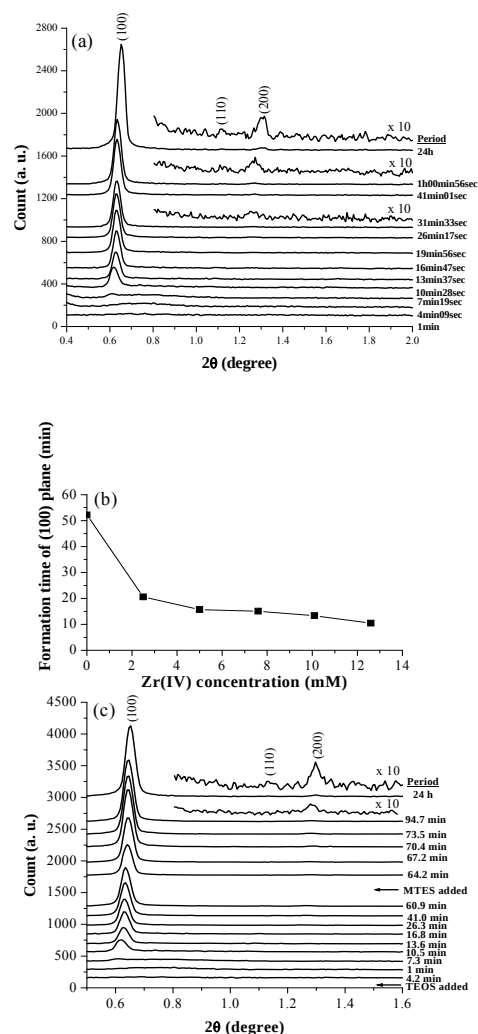


Figure 1. *In-situ* XRD patterns using a synchrotron X-ray radiation source ($\lambda = 1.33344$ Å) of (a) SBA-15 prepared with Zr(IV) ions, and (b) the effect of Zr(IV) concentration on the time (τ) of first appearance of the diffraction peak. (c) the effect of MTES on SBA-15 self-assembly process.