A Simple One-pot Route to Synthesize Mesoporous Silicas SBA-15 Functionalized with Exceptional High Loadings of Pendant Carboxylic Acid Groups

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Functionalization of mesoporous silica materials with organic groups has opened new possibility for their various applications. Since the content of organic groups is a key factor that determines many important properties of the hybrid materials, such as adsorption capacity for metal ions, enhanced hydrothermal stability, and surface reactivity and hydrophobicity, [1,2] synthesis of ordered mesoporous materials with a high content of organic functional groups uniformly distributed over the ordered structure is highly desirable. Relatively few studies have focused on the preparation of mesoporous materials functionalized with carboxylic acid groups (–COOH).

Here we report a simple one-pot synthesis of ordered mesoporous silica SBA-15 with high loadings of pendant carboxylic acid groups, up to 50 mol% of the silicon sites without degradation of ordered structures, via co-condensation of a commercially available organosilane with carboxylate groups, carboxyethylsilanetriol sodium salt (CES), and TEOS under acidic conditions templated by triblock copolymer Pluronic P123.

Figure 1 shows the powder XRD patterns of template extracted –COOH functionalized SBA-15 silica materials. All the samples, up to a CES/(CES + TEOS) molar ratio of 60%, exhibited three well-resolved XRD diffraction peaks in the region of 2θ = 0.5–2.5°, which can be indexed to the (100), (110), and (200) diffractions, characteristic of the 2D *p6mm* hexagonal symmetry. The peak positions for CAR-20 and CAR-30 remained constant after the solvent extraction process, suggesting high stability of the materials (Table 1). The XRD results demonstrated that as high as 60 mol% CES can be incorporated in the initial synthesis mixture without the expense of the integrity and stability of pore structure of the final materials. Unfortunately, a CES loading over 60% can not lead to a powdered sample. Although it has been claimed that a loading of vinyl functionalization of 62% was achieved in mesoporous silica synthesized under basic conditions, the material exhibited only one weak and broad XRD diffraction peak. Besides, in the present case CES contains a larger organic group than vinylsilane, which is not beneficial to self-assembly.

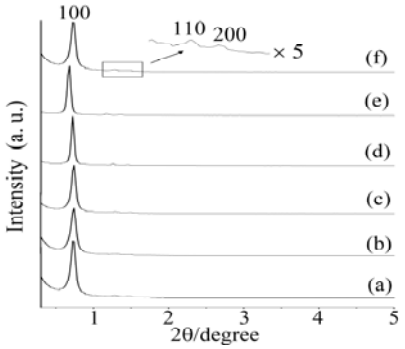

Fig. 1: XRD patterns of template-extracted CAR-*x*, where *x* represents the –COOH content, x = (a) 15, (b) 20, (c) 30, (d) 40, (e) 50, and (f) 60. XRD patterns were collected on Wiggler-A beamline (λ = 0.133367 nm) at the National Synchrotron Radiation Research Center in Taiwan.

The TEM images (Fig. 2) of the CAR-50 sample clearly show a well-ordered 2-D hexagonal (*p6mm*) mesostructure of this sample.

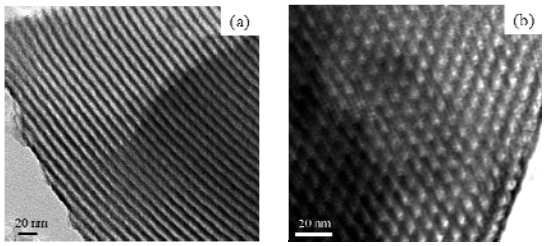

Fig. 2: TEM images of template-extracted CAR-50: (a) in the direction perpendicular to the pore axis and (b) in the direction of the pore axis. The TEM images were acquired on a JEOL JEM 2010 microscope operating at 200 kV.

In conclusion, well-ordered mesoporous silicas SBA-15 functionalized with high loadings of carboxylic acid groups have been prepared via co-condensation of TEOS and carboxyethylsilanetriol sodium salt using triblock polymer Pluronic P123 as the structure-directing agent under acidic conditions. With such a high density of carboxylic acid groups in an ordered mesoporous material, new opportunities for a variety of applications such as in the field of catalysis, adsorption, and ion-exchange for these materials can be visualized.

References

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