Direct Synthesis of Zr-containing Hybrid Periodic Mesoporous Organosilicas with Tunable Zirconium Conten

Shang-Ru Zhai, Sung Soo Park, Mina Park, Md. Habib Ullah, Chang-Sik Ha

Highly ordered Zr-containing periodic mesoporous organosilicas (ZrPMO) with different Zr/Si ratios were successfully synthesized, for the first time, by employing a ZrOCl2/NaCl combination as the promoting agent and by simply adjusting the molar ratio of the zirconium species to the organosilica precursor; no addition of mineral acids was necessary. The effect of preparation parameters on the structural and textural properties were carefully investigated by using different ratios of NaCl/Si and Zr/Si. It was found that both salts are essential for this system and highly ordered ZrPMOs can be prepared within fairly wide Si/Zr ratios (5–100) while keeping the NaCl/Si ratio constant. To prove the effectiveness of this synthetic pathway with a higher Zr incorporation, ZrPMO materials were also synthesized under strongly acidic conditions for the purpose of comparison. The synthesized ZrPMO materials were thoroughly characterized by ICP-AES, SAXS, N2 sorption, TEM, SEM, 13C CP/29Si MAS NMR spectroscopy, XPS, and TGA. Elemental analyses show that the amount of Zr incorporated into ZrPMO, which was synthesized under mild conditions, is greater than that obtained in a strongly acidic environment, and the Zr content, with a Si/Zr ratio up to 12, is close to that in the initial gel composition. A plausible assembly mechanism based on the synergistic effect of both “nonhydrolyzable” (NaCl) and “hydrolyzable” (ZrOCl2) inorganic salts was discussed in detail, where the “salting out” effect and self-generated acidity from both inorganic salts, respectively, are believed to be key factors for the formation of ordered SBA-15-type ZrPMO materials under the synthetic conditions.