L15 The high-temperature synthesis of aluminosilicates.

Ordered mesoporous SBA-15 analogs with different Si/Al ratios were successfully prepared in a two-step process from self-assembly of ZSM-5 nanoseeds at high temperature in mildly acidic media (473 K, pH 3.5). The obtained products were characterized as SAXS, XRD, N2 sorption, FTIR, TEM, NH3-TPD, AAS and ICP. The results show that the initial Si/Al molar ratio of ZSM-5 precursors strongly affects the final materials' properties. A highly condensed, well-ordered mesoporous SBA-15 analog with improved hydrothermal stability and acidic properties can be prepared from low aluminum containing ZSM-5 precursors (Si/Al $\geq$ 20). Reducing the initial Si/Al molar ratio to 10, however, leads to the formation of a disordered mesoporous SBA-15 type material accompanied by degraded textural and acidic properties. The gas phase cracking of cumene, carried out as probe reaction to evaluate Brønsted acidity, reveals that an increased density of Brønsted acid sites has been achieved over the SBA-15 analogs compared to conventional Al-SBA-15 due to the preservation of zeolite building units in the mesopore walls of the SBA-15 analogs.

Zeolites are a unique class of crystalline aluminosilicates that are widely used as catalysts in oil refining and petrochemical industry. The exceptional performance of zeolites primarily stems from their strong Brønsted acidity, hydrothermal stability and uniform micropores of molecular dimensions (typically 0.25–1 nm) [1,2]. Despite their great success, zeolite based catalysts have one main drawback. As one side effect of micropores, zeolites often suffer from internal diffusion limitations particularly when large molecules are involved. Thus, the efficiency in conversion of bulky molecules, e.g., heavy oils might be low because of the restricted access to pores and the slow molecular transport o and from active sites of zeolites. In order to overcome these mass transfer limitations, ordered mesoporous materials (OMMs) with regular mesopores in the range of 2–30 nm have been developed.

The diffusion regime in OMMs is typically Knudsen diffusion, whose diffusivity is several orders of magnitude higher than that of "configurational" diffusion inside micropores of zeolites [3]. Unfortunately, OMMs fail to mimic the key characteristics of zeolites, *i.e.*, strong intrinsic acidity and high hydrothermal stability, owing to the non-crystalline nature of mesopore walls, which severely hinders their practical applications. Accordingly, the introduction of zeolite building units into mesopore walls by using zeolite seeds as building block to construct a mesostructure in a two-step process has been extensively studied [4,5].

Zeolite nanoseeds, also known as precursors or protozeolitic nanoparticles which are presumed to consist of zeolite building units, can be prepared by shortening the hydrothermal treatment time required for evolution of classical zeolite crystals. The use of zeolite precursors for the assembly with triblock copolymer Pluronic P123 as a structure directing agent in strongly acidic media has led to the formation of ordered mesoporous SBA-15 analogs with improved hydrothermal stability and acidic properties [4–8]. The reason for such improvements is not clear, but the retention of zeolite building units in the mesopore walls is thought to play an important role. However, most of these studies were carried out in strongly acidic media at mild temperatures (typically 373–423 K), which resulted in low incorporated aluminum and imperfectly condensed mesopore walls. Consequently, the hydrothermal stability and acidic properties of the known SBA-15 analogs, e.g., MAS-9 [6] or MSU-S/H [8] are still inferior to those of zeolites, being unsatisfactory for industrial applications. Recently, we developed an effective method for further improving the hydrothermal stability and acidic properties of ordered mesoporous SBA-15 analogs assembled from ZSM-5 precursors (denoted as SAZ) by high-temperature synthesis and pH adjustment [9]. The ordered mesostructure of SAZ materials was well preserved even upon steaming at 1073 K for 4 h with little loss in the specific BET surface area by 11% only, while their acidic properties were substantially enhanced in terms of both number and strength of acid sites.

Figure 1. (**a**) Small angle X-ray Scattering (SAXS); (**b**) X-ray diffraction (XRD) patterns; and (**c**) Fourier transform infrared (FTIR) spectra of SAZ materials, Al-SBA-15 and H-ZSM-5.

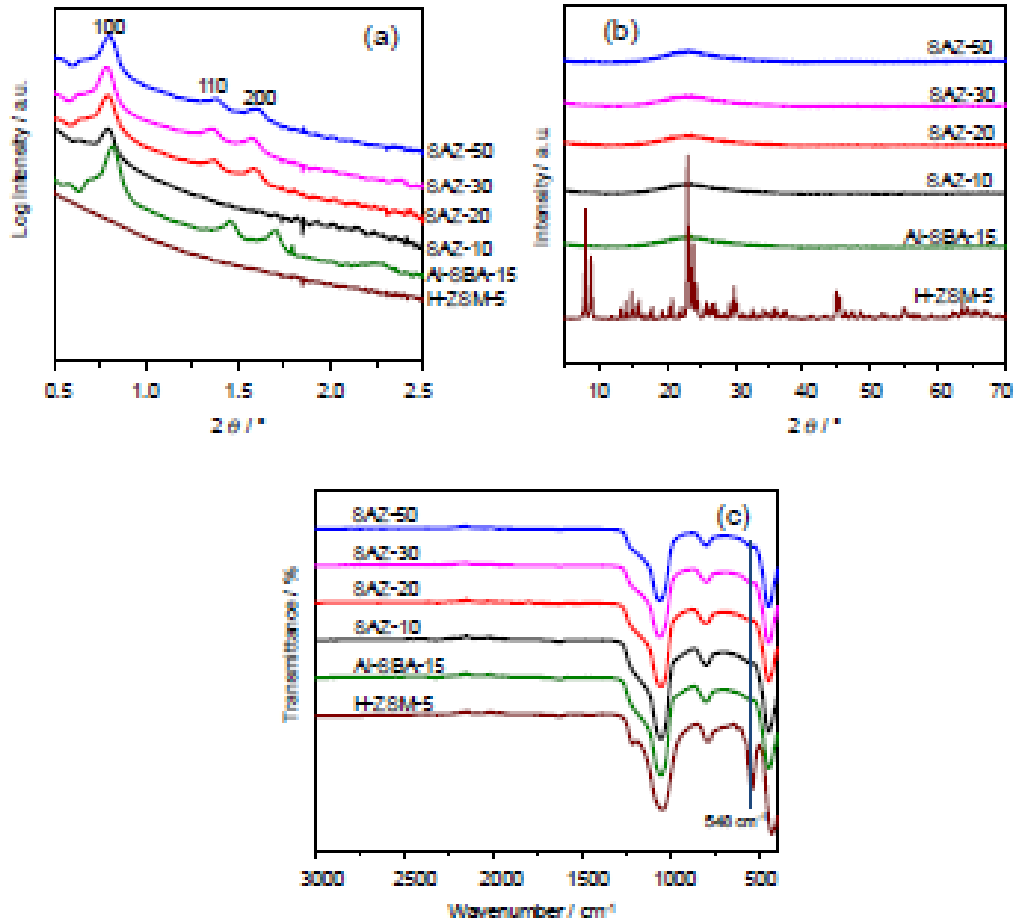


Figure 2. (**a**) N_2 sorption isotherms; and (**b**) corresponding pore size distributions of SAZ and Al-SBA-15 materials.

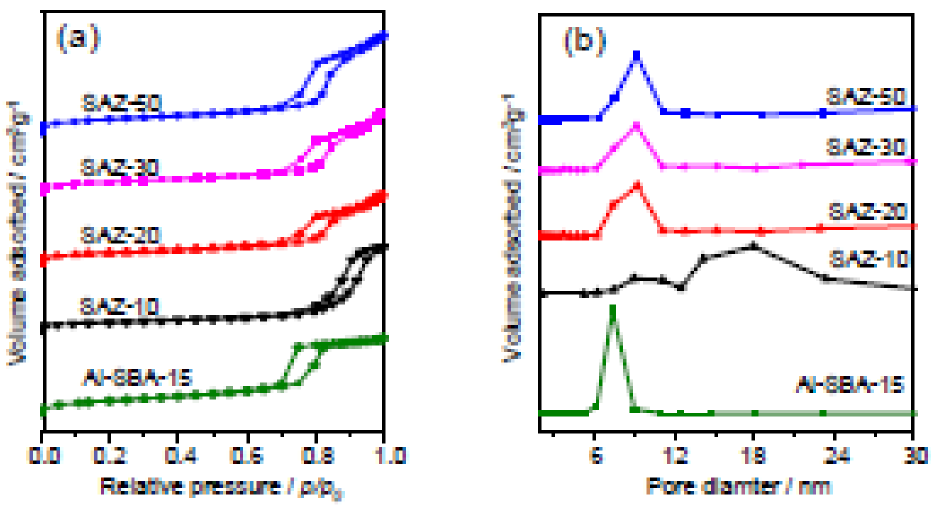
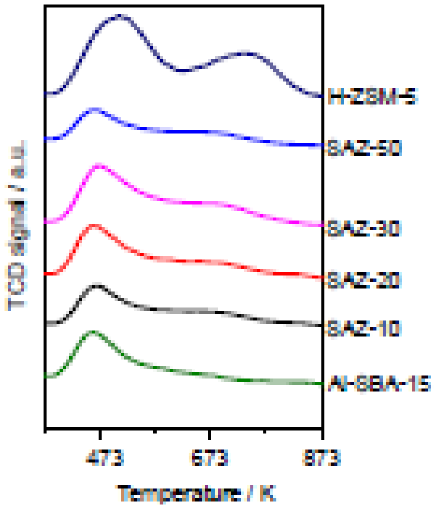


Figure 3. Temperature-programmed desorption of ammonia (NH_3-TPD) profiles of SAZ solids compared to reference samples Al-SBA-15 and H-ZSM-5.



References:

Xuan Hoan Vu, Reinhard Eckelt, Udo Armbruster and Andreas Martin. High-Temperature Synthesis of Ordered Mesoporous Aluminosilicates from ZSM-5 Nanoseeds with Improved Acidic Properties // Nanomaterials 2014, 4, 712-725; doi:10.3390/nano4030712