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Growth of zeolite KSO1 on calcined kaolin microspheres

Mingcan Xu, Mojie Cheng, Xiumei Liu, Dali Tan and Xinhe Bao*

*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, Dalian 116023, P R China. E-mail: xhbao@ms.dicp.ac.cn*

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Zeolite KSO1 was successfully synthesized on calcined kaolin microspheres (*ca.* 60–80 μm) *in situ*, and characterized by powder X-ray diffraction, scanning electronic microscopy and nuclear magnetic resonance spectroscopy.

In recent years, *in situ* synthesis of zeolites on various supports has attracted considerable attention. A variety of zeolites have been grown on ceramic supports,[1] metal substrates,[2] glasses[3] and even a mercury surface.[4] High selectivity[5] and poison resistance[6] of the supported zeolite catalysts have been reported. The limited available surface area, however, is a serious drawback. If a zeolite can be synthesized *in situ* on desired microspheres, the effective surface area will increase greatly. Up to now, no reports concerning the *in situ* synthesis of zeolites on microspheres have been published. In this communication, we report on the *in situ* synthesis of zeolite KSO1 on calcined kaolin microspheres.

The *in situ* synthesis was carried out under hydrothermal conditions according to the following procedure. At first, uniform microspheres (GSS600) were obtained by flotation with deionized water from calcined kaolin microspheres(GSS), and then calcined at 600 °C for 2 h. A clear aqueous solution with the composition in terms of molar ratios of 6 : 5 : 36 ($SiO_2 : Na_2O : H_2O$) was prepared by the addition of sodium hydroxide to silica sol. GSS600 (10 g) was added to the solution, which was then heated at 100 °C for 30 min with agitation. Then a sodium aluminate solution, obtained from deionized water, sodium hydroxide and aluminium sulfate, was slowly added to the above mixture with stirring. Thereafter, a definite quantity of sulfuric acid aqueous solution was immediately added with agitation to form a gel with the final composition in terms of molar ratios 1 : 16 : 7.8 : 393 ($Al_2O_3 : SiO_2 : Na_2O : H_2O$). Finally, the mixture obtained was maintained at 100 °C for 40 h. The product (ICK) was separated and dried at about 120°C.

All the above steps are derived from an idea to form a (so-called) double-layered gel on the microsphere. As described above, just after the addition of the sodium aluminate solution and before complete mixing, the medium most closely surrounding the microsphere was silicate solution, and outside the silicate solution was aluminosilicate solution. During the addition of sulfuric acid, a complex gel might form around the microsphere, with the inner portion near the surface of the microsphere being silicate gel, and the outer portion being aluminosilicate gel. We refer to this complex gel as a double-layered gel.

Zeolite KSO1 is often found in the synthesis of faujasite Y,[7,8] and can be used as a catalyst.[9] Kaolin, a name long used for china clay, is essentially an aggregation of book-shaped units of sheets of the clay mineral kaolinite,[10] and also contains some mica, quartz and other oxides. After calcination, kaolinite is

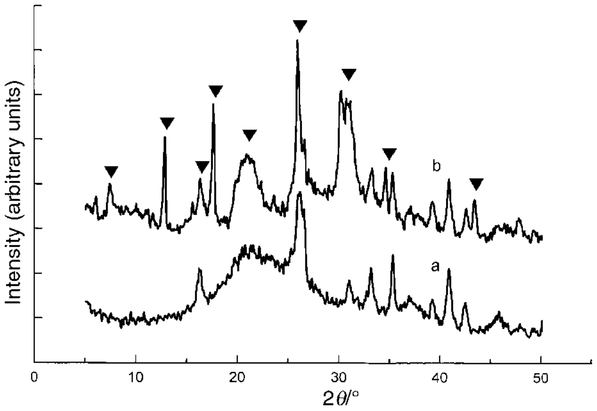

Fig. 1 XRD patterns of GSS (a) and ICK (b). The characteristic peaks of zeolite KSO1 are indicated by ▼. The X-ray diffraction data were obtained on a Rigaku D/MAX-γb diffractometer using Cu-Kα radiation, 40 kV, 100 mA with a scanning speed of 5° (2θ) min^{-1}.

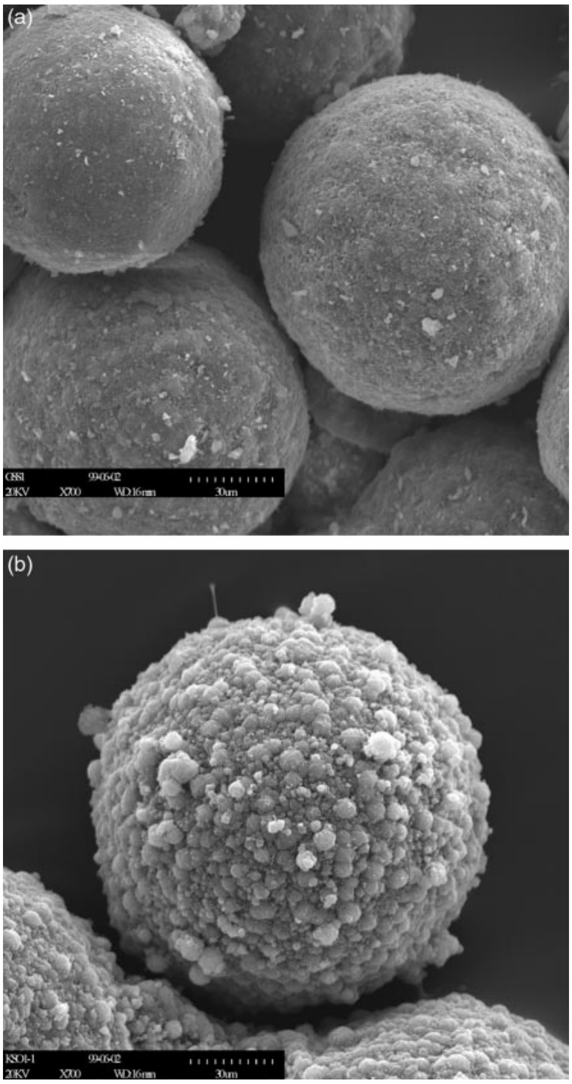

Fig. 2 SEM pictures of GSS (a) and ICK (b) obtained on an S3200N (HITACHI) scanning electronic microscope.

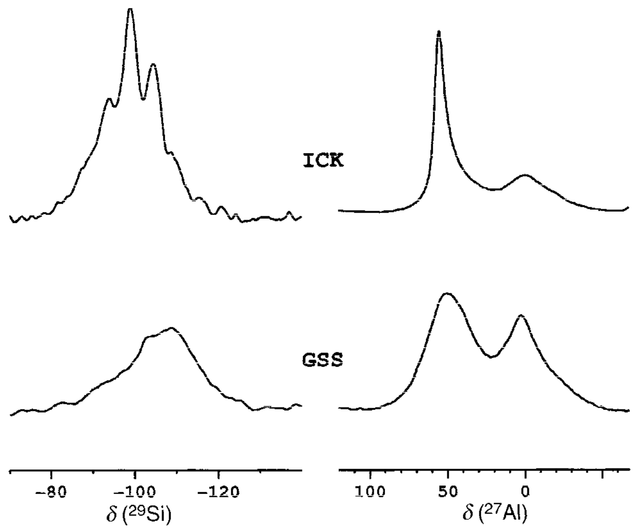

Fig. 3 NMR spectra of GSS and ICK (obtained on a Bruker DRX 400 multinuclear spectrometer after the samples had been kept in a desiccator containing saturated ammonium chloride aqueous solution for at least 24 h). The ^{29}Si MAS NMR spectrum was recorded using a $\pi/8$ pulse at 104.2 MHz with the sample in a rotator spinning at 4000 cycles s^{-1}, and the ^{27}Al MAS NMR spectrum was recorded using a $\pi/12$ pulse at 79.5 MHz with the sample in a rotator spinning at 8000 cycles s^{-1}.

transformed into metakaolinite.[11] In the XRD pattern of GSS [Fig. 1(a)], a broad background, characteristic of amorphous materials, was observed. Apart from the peaks attributed to the existence of mica and quartz impurities, no peaks representing crystalline kaolinite were present. After *in situ* crystallization, the XRD pattern of the zeolite KSO1[9] clearly appeared in ICK [Fig. 1(b)], accompanied by the background from calcined kaolin microspheres, while no peak representing other zeolites could be identified.

The scanning electronic microscopy (SEM) pictures unequivocally interpret the XRD results that zeolite KSO1 was synthesized *in situ* on the calcined kaolin microspheres. Compared with GSS in Fig. 2(a), ICK in Fig. 2(b) appears to be coated with a layer of serried crystallites. The spherical crystallites were closely packed on the surface of the calcined kaolin microspheres, and no other kind of crystallite was observed.

In Fig. 3, the ^{29}Si MAS NMR spectrum of GSS shows only a broad resonance signal at *ca.* −106 ppm which is commonly due to amorphous materials. In spite of the existence of the background from GSS, ICK (Fig. 3) exhibited typical zeolite resonance signals in the range from −80 ppm to −110 ppm. The ^{27}Al MAS NMR spectrum of GSS shows two broad resonance signals at *ca.* 2.5 ppm and *ca.* 50.7 ppm. The former is normally assigned to 6-coordinated aluminium, while the latter is from 4-coordinated and 5-coordinated aluminium.[12] The spectrum from the sample ICK shows a sharp resonance signal at *ca.* 55 ppm, revealing the existence of 4-coordinated aluminium in the zeolite framework. Because of the contribution from 4-coordinated and 5-coordinated aluminium of GSS, this resonance signal appeared at slightly higher field than that of the pure zeolite.

Our success in the *in situ* synthesis of zeolite KSO1 on calcined kaolin microspheres may pave the way for further research on *in situ* synthesizing zeolites on microspheres.

Notes and references

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