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One-pot synthesis of superacid catalytic material SO_4^{2-}/ZrO_2-SiO_2 with thermostable well-ordered mesoporous structure

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ABSTRACT

A superacid mesostructured catalyst was directly synthesized by adding sulfuric acid to mesoporous zirconia–silica synthesis mixtures, and was characterized by HRTEM, XRD, UV–Vis, nitrogen sorption, NH_3–TPD, and Pyridine–FTIR. The XRD patterns and electron diffraction micrographs of the calcined samples showed the ordered mesoporous structure and tetragonal crystalline in frameworks. The ammonia TPD, pyridine *in situ* FTIR, and paraffin isomerization illustrated a new acidic property of the samples. The synthesis of the mesoporous materials, which have stable crystalline frameworks, high surface area, and strong acidity, is very likely to have important technological implications for catalytic reactions of large molecules.

1. Introduction

Since ordered mesoporous aluminosilicate materials, such as MCM41s, were synthesized in 1992 [1], mesoporous molecular sieves have attracted strong interest because of their potential applications in advanced catalytically materials and adsorbents. The crucial problem is that the mesoporous aluminosilicate represents poor hydrothermal stability, either in stream or in hot water. As a result, the application of new materials has been limited [2]. Subsequently, researchers used a triblock copolymer to organize the structure of a polymeric silica precursor template to form new mesoporous silica denoted SBA-15 with periodic 5–30 nm pores. SBA-15 has more regular structure and thicker walls than MCM-41, resulting in higher stability, but low catalytic activity due to its pure silica frameworks [3]. Compared with crystalline zeolites, mesoporous materials exhibited insufficient hydrothermal stability and acidity. This difference draws many researchers to improve the framework crystallinity and acidity for practical applications. Recently, significant progresses in developing new mesoporous structures have been made [4,5–8]. However, properties of the parent mesostructured materials, including so-called mesoporous zeolites, were not comparable with that of crystalline zeolites used in the industry [9].

While various attempts have been reported to improve framework crystallinity of the mesoporous aluminosilicate materials, the relatively low acidity, unsatisfactory pore structure, and thermal stability have not been completely resolved. On the other hand, the mesoporous materials containing zirconium have received considerable attention in heterogeneous catalysis because of their potential acid properties [10–12]. The mesoporous structure of these materials is unstable in thermal treatment and will collapse when at temperatures above 600 °C. Adding sulfate anions to the material at the precipitation stage or through post-treatment of the formed mesoporous phase using sulfuric acid or ammonium sulfate plays an important role for stabilizing the mesoporous structure of ZrO_2 and enhancing the acidic properties. Several practices have succeeded in introducing zirconium into the framework of molecular sieves during synthesis, but the material has a ratio of Zr/Si lower than 0.025 [13]. Thermally stable mesoporous materials based on silica-stabilized zirconia were synthesized in two steps using hexadecyl trimethyl ammonium bromide as a template. These silica-stabilized materials have still an amorphous phase up to 600 °C, in which the strength of most acid sites is similar to that in conventional SO_4^{2-}/ZrO_2. This process partly improves acidity and/or hydrothermal stability [14]. Recently, we reported a new strategy to directly synthesis Zr-SBA-15 using a triblock copolymer and hexadecyl trimethyl ammonium bromide (CTAB) as co-templates, and then sulfated to obtain a mesostructured SO_4^{2-}/ZrO_2 material with high surface area and strong acidity used in paraffin isomerization [15]. Herein, we report a direct synthesis route to mesoporous superacid catalysts $SO_4^{2-}/ZrO_2–SiO_2$ (denoted as MSC_x, here x is Zr/Si ratio) with ordered mesoporous structure and crystalline frameworks by one-pot method.

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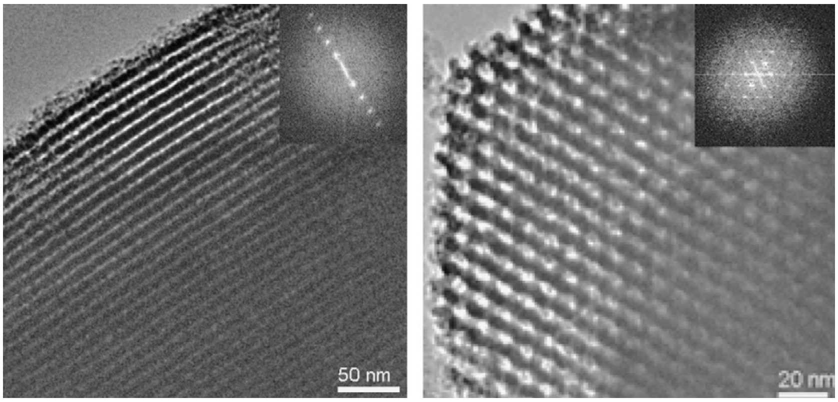

Fig. 1. TEM images of the calcined mesoporous catalyst MSC_x ($x = 1.1$). Insets: the corresponding electron diffraction pattern.

2. Experimental

In a typical synthesis, 15 ml of alcohol solution containing 1.63 g CTAB were fully mixed with 40 ml of alcohol solution containing 4.4 g $Zr(NO_3)_4 \cdot 3H_2O$ and then transferred into Teflon-lined autoclave and preheated at 110 °C for 3.5 h to obtain sample-I. The 20 ml of 1 mol/l H_2SO_4 solution were mixed with 20 ml of 2 mol/l HCl solution containing 1 g triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO_{20}–PO_{70}–EO_{20}, P_{123}, Aldrich), 2.3 ml of tetraethyl orthosilicate (TEOS) were added in the mixture and stirred for 3 h at 40 °C to obtain sample-II. Sample-I was mixed with sample-II under stirring. The final mixture was stirred continuously for another 3 h and then transferred into Teflon-lined autoclave at 100 °C for 48 h. The as-synthesized solid was filtered, washed with distilled water and dried, and calcined in air flow at 600 °C for 3 h to obtain MSC. The MSC_x ($x = 0.1$–3.0) were synthesized in the same processing and characterized by the techniques such as high-resolution transmission electron microscopy (HRTEM), field emission scanning electron microscopy (FESEM), X-ray powder diffraction (XRD), UV–Vis, N_2 adsorption isotherm, and the temperature-programmed desorption of ammonia.

3. Results and discussion

The HRTEM images of the calcined MSC sample (Fig. 1) show well-ordered hexagonal arrays of mesopores with one-dimensional channels and unambiguously confirm that the hexagonal pore structure of the SBA-15 was retained. The corresponding electron diffraction patterns (insets of Fig. 1) indicate that the final product was a mesoporous material with a polycrystalline framework. During the calcination, tetragonal ZrO_2 began to take into form, and at the same time it incorporated and coordinated in the silica framework. The existence of tetrahedral ZrO_2 in silica framework was suggested by ^{29}Si NMR spectra [15]. A well-ordered mesoporous material with partial crystalline frameworks is well supported by a small-angel XRD peak at $2\theta = 0.9°$ and the wide-angel XRD peaks corresponding to the ZrO_2 tetragonal structure (inset in Fig. 2). One diffraction peak in the low angle region ($2\theta \leqslant 5$) is visible indicating that MSC has a long-range hexagonal ordering. Bulk MSC shows the pure tetragonal phase of zirconia in the ordinary region ($2\theta = 30$–50) rather than a monoclinic zirconia phase. As indicated by SEM (not shown) and HRTEM images, no aggregated ZrO_2 particles can be observed. The corresponding electron diffraction (inset in Fig. 1) indicated that the final product was a mesoporous material with a crystalline framework. The porosity of the MSC materials was studied by

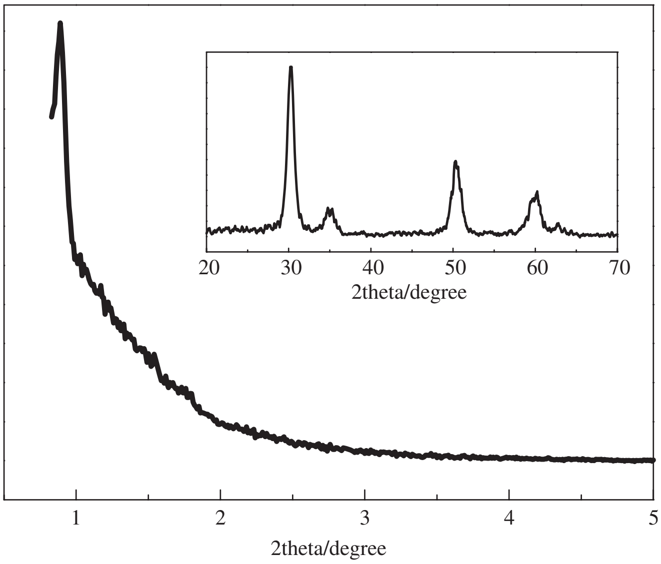

Fig. 2. XRD pattern of the calcined mesoporous catalyst MSC_x ($x = 1.1$).

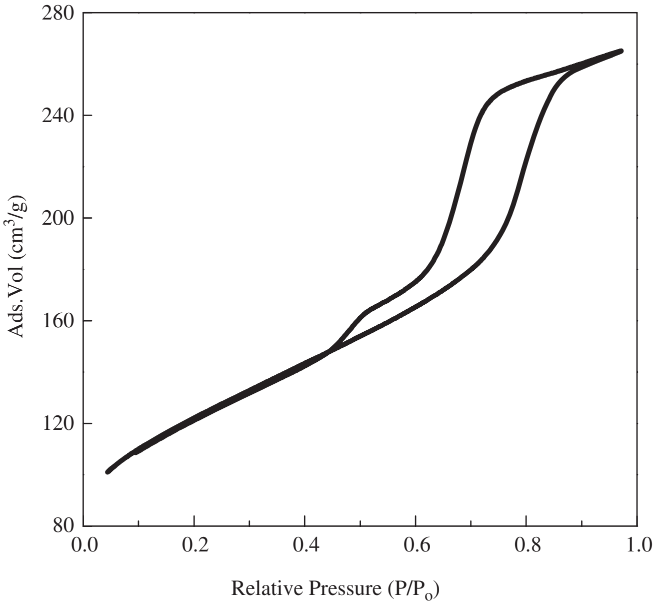

Fig. 3. N_2 adsorption isotherm of the calcined mesoporous MSC_x ($x = 1.1$).