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Hierarchical zeolites prepared by organosilane templating: A study of the synthesis mechanism and catalytic activity

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ABSTRACT

The crystallization of hierarchical ZSM-5 in the presence of the organosilane octadecyl-dimethyl-(3-trimethoxysilyl-propyl)-ammonium chloride as the mesoporogen was investigated as a function of time and temperature. The synthesis by this method proceeds in two steps. The rapid formation of a predominantly amorphous disordered mesoporous aluminosilicate precursor phase is followed by the formation of globular highly mesoporous zeolite particles involving dissolution of the precursor phase. It is difficult to completely convert the initial phase into the final hierarchical zeolite. This limits the amount of aluminium built into the MFI network and the resulting Brønsted acidity. In the presence of iron, more crystalline hierarchical zeolite is obtained. These Fe-containing zeolites are excellent catalysts for the selective oxidation of benzene to phenol. Their hierarchical pore structure leads to higher reaction rates due to increased mass transfer and increased catalyst longevity despite more substantial coke formation.

1. Introduction

Hierarchical zeolites and large pore silicates can overcome the pore size constraints and mass transfer limitations by decreasing diffusion path lengths [1–3]. Introducing substantial mesoporosity in zeolite crystals has become a very active research area in recent years. Among the novel approaches to arrive at mesoporous zeolites are carbon black scaffolding, polymer templating, desilication and agglomeration of nano-sized zeolites [3–7]. The unsuccessful initial attempts to combine templates for zeolite growth and the growth of ordered mesoporous silicas can be overcome by covalently linking mesoporogens to the growing zeolite crystal surface as shown by Choi et al. [8–10]. By using a trimethoxysilyl group in a mesoporogen such as cetyltrimethylammonium, Choi et al. [8] obtained highly mesoporous MFI type zeolite with improved catalytic activity. Recently, the benefit of this approach for the preparation of much improved [Fe]ZSM-5 catalysts for the selective oxidation of benzene to phenol by nitrous oxide was demonstrated [11]. The high connectivity between micropores and mesopores or, alternatively stated, the very small microporous domains in these hierarchical zeolites resulted in superior catalytic performance when compared to conventional microporous catalysts. Despite the ease of the organosilane templating method, the details of the synthesis mechanism and how the use of the organosilane template affects the catalytic properties remain to be addressed. Herein we report on our detailed investigations of the synthesis mechanism of HZSM-5 and [Fe]ZSM-5 templated by tetrapropylammonium bromide as the microporogen and octadecyl-dimethyl-(3-trimethoxysilyl-propyl)-ammonium chloride as the organosilane mesoporogen. We will follow the morphology, texture and catalytic properties of the materials as a function of the hydrothermal conditions (time and temperature). The acidic properties of the hierarchical HZSM-5 zeolites are investigated by Brønsted acid site titration and n-heptane hydroconversion. The catalytic performance of the Fe-containing zeolites will be compared by using nitrous oxide decomposition and selective oxidation of benzene to phenol.

2. Experimental

2.1. Synthesis of mesoZSM-5

MFI-type zeolites with substantial mesoporosity were synthesized using the hydrothermal procedure involving organosilanes as described by Choi et al. [8]. Zeolites were grown at different crystallization temperatures and times. In a typical procedure

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0.21 g sodium aluminate, 4.2 g tetrapropylammonium bromide and 1.2 g sodium hydroxide were dissolved in 202.5 ml of demineralized water. A second solution was made by mixing 12.9 g tetraethylorthosilicate (TEOS) with 2.07 g octadecyl-(3-trimethoxysilylpropyl)-ammonium chloride (TPOAC) in methanol (60% w/w). The silicate solution was added dropwise to the first solution yielding a synthesis gel with the molar composition NaO/AlO_2/TPABr/TPOAC/Si/H_2O = 11/1/5.3/0.9/20/3750. The gel was stirred at room temperature for 2 h and transferred to a Teflon lined stainless steel autoclave thereafter. The mixtures were hydrothermally treated in a static autoclave followed by rapid quenching. Products were recovered by filtration and washed with copious amounts of demi water and subsequently dried overnight at 100 °C. Organic templates were removed by calcination. Samples were heated in a flow of nitrogen (100 ml/min) at a heating rate of 1 °C/min to 550 °C, followed by exposure to artificial air at the same temperature for 4 h. Samples are denoted by mesoZSM-5(*T*, *y*) with *T* being the crystallization temperature and *y* the crystallization time in h. To convert the samples to the H^+ form they were ion exchanged three times with 1 M NH_4NO_3 for 8 h at 90 °C followed by calcination at 550 °C. A second set of samples was grown at 150 °C for 120 h at varying ratios of Si/TPOAC between 240 and 12. These samples are denoted by mesoZSM-5(*T*, 120, *z*) with *z* the ratio of Si/TPOAC. A reference sample denoted as TMS (TPOAC templated mesoporous silicate) was grown without TPABr by hydrothermal treatment at 125 °C for 24 h.

2.2. Synthesis of meso[Fe]ZSM-5

For the iron containing mesoporous Fe/ZSM-5 an adapted procedure described by Xin et al. was used [11]. Typically, 0.21 g sodium aluminate, 4.2 g of tetrapropylammonium bromide and 1.2 g sodium hydroxide were dissolved in 192.5 ml demineralized water. An iron precursor solution was made by dissolving 0.13 g of $Fe(NO_3)_3{\cdot}9H_2O$ in 10 ml demineralized water. A silicon precursor solution was made by mixing 12.9 g TEOS and 2.07 g TPOAC. Under vigorous stirring this solution was added dropwise to the first solution followed by the addition of the iron precursor solution. The resulting yellowish suspension was stirred at room temperature for 2 h and transferred to a Teflon lined stainless steel autoclave. Samples were hydrothermally treated in a static autoclave at 150 °C. The reaction was rapidly quenched and the samples were recovered by filtration and washed with copious amounts of demineralized water. Samples were dried overnight at 100 °C. The template was removed by Soxhlet extraction with methanol for 12 h followed by calcination. Samples were heated in a flow of nitrogen to 550 °C at a heating rate of 2 °C/min, followed by air calcination at 550 °C for 6 h. To convert the zeolites to the H^+ form they were three times ion exchanged with 1 M NH_4NO_3 at 90 °C for 8 h followed by calcination at 550 °C. Prior to the catalytic testing samples were steamed at 700 °C for 3 h in a flow of 10 vol% steam in nitrogen at a flow rate of 50 ml/min. Samples are denoted as meso[Fe]ZSM-5(150, *y*) with *y* the crystallization time in h.

2.3. Characterization

The metal content of the samples was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Spectro CIROS CCD spectrometer equipped with a free-running 27.12 MHz generator at 1400 W. Prior to the measurement samples were dissolved in a mixture of $HF/HNO_3/H_2O$ (1:1:1).

UV–vis spectra were recorded on a Shimadzu UV-2401 PC spectrometer in diffuse-reflectance mode with a 60 mm integrating sphere. $BaSO_4$ was used as the reference. The spectra were transformed into the Kubelka–Munk function and subsequently deconvoluted into subbands by standard peak fitting software.

Infrared spectra were recorded on a Nicolet Avatar 360 spectrometer with a KBr pellet (1 mg of zeolite in 100 mg of KBr). IR crystallinities were determined by the ratio of the intensities of the band at 450 cm^{-1} and 550 cm^{-1} compared to a ZSM-5 reference standard [12,13].

XRD patterns were recorded on a Bruker D4 Endeavor powder diffraction system using Cu Kα radiation with a scanning speed of 0.0057° min^{-1} in the range of $0.5° \leq 2\theta \leq 5°$ and 0.01° min^{-1} in the range of $5° \leq 2\theta \leq 60°$. XRD crystallinities were determined using the Bruker TOPAS 3.0 software.

Nitrogen sorption isotherms were measured at −196 °C on a Micromeritics ASAP2020 system in static measurement mode. The samples were outgassed at 400 °C for 8 h prior to the sorption measurements. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area (S_{BET}) from the adsorption data obtained (p/p_0 = 0.05–0.25). The mesopore volume (V_{meso}) and mesopore size distribution were calculated using the Barrett–Joyner–Halenda (BJH) method on the adsorption branch of the isotherm. The micropore area (S_{mic}) and micropore volume (V_{mic}) were calculated from the t-plot curve at thickness range between 3.5 and 5.4 Å [14,15]. The micropore size distribution was calculated using the Horvath–Kawazoe (HK) method for slit pore geometries applying Saito–Foley (SF) correction [16].

Transmission electron micrographs were obtained with a FEI Tecnai 20 instrument at an electron acceleration voltage of 200 kV. Typically, a small amount of sample was suspended in ethanol, sonicated and dispersed over a Cu grid with a holey carbon film.

Scanning electron microscopy (SEM) was performed using a Philips environmental scanning electron microscope FEIXL-30 ESEM FEG in high-vacuum mode at low voltage.

Magic angle spinning (MAS) ^{27}Al single pulse NMR spectra were recorded on a Bruker Avance DMX-500 NMR spectrometer equipped with a 2.5 MAS probe head operating at a magnetic field of 11.7 T (the Al resonance frequency at this field is 130.3 MHz). The ^{27}Al chemical shift is referred to a saturated $Al(NO_3)_3$ solution. In a typical experiment 10 mg of well-hydrated sample was packed in a 2.5 mm zirconia rotor. The MAS sample rotation speed was 25 kHz. The relaxation time was 1 s and the pulse length was 1 μs.

UV Raman spectra were recorded with a Jobin–Yvon triple stage spectrograph with spectral resolution of 2 cm^{-1}. The laser line at 244 nm of a Coherent Innova 300 Fred laser was used as exciting source with an output of 20 mW. The power of the laser on the samples was about 2 mW.

2.4. FTIR H/D exchange

H/D exchange of hydroxyl groups with perdeuterated benzene was followed in situ by infrared spectroscopy as described elsewhere [17]. Infrared spectra were recorded in transmission mode in a Bruker IFS-113v FTIR spectrometer with a mid-infrared DTGS detector. Typically, a powdered sample was pressed into a self-supporting wafer with a density ρ = 10 mg/cm^2 and placed in an in situ cell. After calcining the catalyst wafer at 550 °C, the catalyst was evacuated to a pressure better than 2×10^{-6} mbar and temperature was lowered to 30 °C. A background spectrum was recorded. Perdeuterobenzene (C_6D_6, Merck, purity 99.96%) was introduced into the cell from a glass ampoule. The total volume of C_6D_6 administered to the cell was 0.33 mmol ±1%, resulting in a pressure of 10 mbar. IR spectra were recorded for different exposure times and temperatures. For each spectrum, 125 scans were accumulated at a resolution of 2 cm^{-1}. Difference spectra were obtained by subtracting the initial spectrum of the dehydrated sample from the spectra after exposure to C_6D_6.