

# Hydrothermal Stability of Meso-microporous Composites and Their Catalytic Cracking Performance

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**Abstract:** Meso-microporous composites show great promise for catalysis because of their variously-sized porous structures. A series of composites containing uniform mesopores and MFI zeolitic channels were prepared by a template-free sol-gel method. The composite containing silicalite-1 structures was found to be much more hydrothermally stable than MCM-41. The composites with ZSM-5 structures showed higher catalytic activity and resistance to deactivation than commercial HZSM-5 in the catalytic cracking reaction of 1,3,5-triisopropylbenzene. The conversion and catalytic cracking product distribution of 1,3,5-triisopropylbenzene depended highly on the mesopore size of the composites. Higher conversions and small molecule cracking products were obtained using composites with smaller mesopores.

**Key words:** meso-microporous composite; MFI zeolite; hydrothermal stability; 1,3,5-triisopropylbenzene; catalytic cracking

Zeolites have been applied widely in many industrial processes such as adsorption and catalysis because of their high surface area, adsorption capacity, ion-exchange capacity, and regular arrays of channels and cavities (0.3–1.5 nm). Their intricate channel structures allow the zeolites to have different types of shape selectivity, i.e., for products, reactants, and transition states, which can be used to direct a given catalytic reaction toward the desired product and avoid undesired side reactions [1]. However, the small pore sizes of zeolites result in diffusion and mass transfer limitations especially in the reactions involving large molecules. Since the discovery of MCM-41 in 1992 [2,3], mesoporous materials have attracted much attention because of their potential use as catalysts and catalyst supports for the conversion of large molecules. Compared to conventional zeolites, mesoporous materials have low hydrothermal stability and acidity, which has been attributed to their amorphous pore walls [4].

Since meso-microporous composites can possibly combine the advantages of variously-sized porous structures, researchers have made many attempts to prepare meso-microporous composites. Pinnavaia et al. [5,6] and Xiao et al. [7,8] used

surfactant to assemble zeolite precursor for synthesizing mesoporous materials with zeolitic walls. Zeolites with mesopores were also fabricated by the addition of different templates such as rigid templates containing carbon nanoparticles [9], carbon nanotubes [10] and carbon aerogels [11,12] or soft templates containing polymers [13,14] and surfactants [15,16] into the zeolite synthesis solution. As to template-free routes to the meso-microporous composite, steaming, acid-leaching dealumination [17], and alkali-leaching desilication [18] of zeolite crystals often generate mesopores with wide size distributions. In our previous work, we developed a template-free sol-gel method to synthesize a series of meso-microporous composites from a zeolite precursor sol. They were found to consist of interconnected worm-like mesopores or intercrystalline mesopores with irregular arrays and their mesopore sizes could be controlled between 2 and 30 nm [19–21]. In this work, we investigated the hydrothermal stability of several meso-microporous composites and their catalytic performance in the cracking reaction of 1,3,5-triisopropylbenzene.

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## 1 Experimental

### 1.1 Preparation of the meso-microporous composites

#### 1.1.1 Preparation of the MFI zeolite precursor sol

In a typical silicalite-1 precursor sol synthesis, 20.4 g of the 20% aqueous solution of tetrapropylammonium hydroxide (TPAOH, Fluka) was added to 16.7 g of tetraethyl orthosilicate (TEOS, 98%, Beijing Yili) under vigorous stirring. To the resulting emulsion, 19.8 g of twice distilled water was added. The resulting emulsion with the molar composition of 1.0TEOS:0.25TPAOH:25H<sub>2</sub>O was stirred at 50 °C for 48 h to form a clear silicalite-1 precursor sol.

25.4 g of the 20% aqueous solution of TPAOH was added to the mixture of 20.8 g of TEOS and 0.4 g of aluminum isopropoxide (Al(*i*-OPr)<sub>3</sub>, 99.5%, Tianjin Jinke) under vigorous stirring at room temperature to obtain a turbid solution with the molar composition of 1.0TEOS:0.02Al(*i*-OPr)<sub>3</sub>:0.25TPAOH:11.3H<sub>2</sub>O. Clear ZSM-5 precursor sol was obtained by stirring the turbid solution at 50 °C for 48 h.

#### 1.1.2 Preparation of the MFI zeolite precursor xerogel

Silicalite-1 and the ZSM-5 precursor sol were transferred to clean glass dishes and dried at 30 °C in a vacuum box at 6.67 kPa until they became xerogels. The silica contents in the silicalite-1 and ZSM-5 xerogels were  $7.0 \times 10^{-3}$  mol/g and  $7.7 \times 10^{-3}$  mol/g, respectively.

#### 1.1.3 Solvo/hydrothermal crystallization of the xerogel

Glycerol ( $\geq 99.0\%$ , Anshan Zhiao), glycol (99.8%, Tianjin Bodi), and twice distilled water were used as media for heat crystallization. A mixture of xerogel and solvent/water (1 SiO<sub>2</sub>:150 solvent/water molar ratio) was transferred into Teflon-lined stainless steel autoclaves and solvo/hydrothermal crystallization was carried out at a certain temperature for 24 h. The solid products were filtered, washed, dried at 30 °C in a vacuum box, and calcined in air at 550 °C for 6 h. The calcined samples were designated S-X-*y* or Z-X-*y* (S and Z indicate silicalite-1 and ZSM-5 xerogels, respectively; X represents the crystallization medium such as G = glycerol, A = glycol, and W = water; *y* is the crystallization temperature). For example, S-G-130 was the sample prepared by crystallizing silicalite-1 xerogel and glycerol at 130 °C. We prepared five meso-microporous composites: S-G-130, Z-G-130, Z-A-130, Z-A-180, and Z-W-100.

### 1.2 Preparation of mesoporous MCM-41

Mesoporous MCM-41 was also synthesized for comparison. 0.3 g of sodium hydroxide (NaOH,  $\geq 96.0\%$ , Tianjin Kemiou)

and 1.7 g of cetyltrimethylammonium bromide (CTAB,  $\geq 99.0\%$ , Shanghai Guoyao) were dissolved in 144 ml of twice distilled water at 40 °C followed by the addition of 8.3 g of TEOS at room temperature. The mixture was stirred for 15 min and transferred into a Teflon-lined stainless steel autoclave to carry out hydrothermal synthesis at 120 °C for 3 d. As-synthesized MCM-41 was filtered, washed, dried, and calcined in air at 550 °C for 6 h.

### 1.3 Characterization of the samples

The particle size distribution of the precursor sol was measured using a N4 plus laser scattering particle meter (Coulter) equipped with a 10 mW He-Ne laser. X-ray diffraction (XRD) characterization was performed using a Rigaku D/max-2500PC X-ray diffractometer with a copper target at 40 kV and 30 mA ( $2\theta = 1^\circ\text{--}10^\circ$ ) or 100 mA ( $2\theta = 5^\circ\text{--}50^\circ$ ) with the step size of 0.02°. Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet Impact 410 FTIR spectrometer. A mixture of the sample and KBr was pressed into a thin wafer before the IR measurement. All IR spectra were measured under the following conditions: resolution of 4 cm<sup>-1</sup>, scan time of 32, and scan range from 400 to 4000 cm<sup>-1</sup>. N<sub>2</sub> adsorption/desorption isotherms of the samples were measured on a Coulter Omnisorp-100CX apparatus at -196 °C. The solid samples were first degassed at 350 °C under high vacuum ( $1.33 \times 10^{-4}$  Pa) for 3 h to remove adsorbed impurities from the pores of the samples before the isotherms were recorded. Mesopore and micropore size distributions were determined using BJH method from desorption branch and HK method from adsorption branch, respectively.

### 1.4 Hydrothermal stability and catalytic cracking performance

0.1 g of the calcined sample and 20 g of twice distilled water in a Teflon-lined stainless steel autoclave were heated at 180 °C for 12 h to test hydrothermal stability. The catalytic cracking reaction of 1,3,5-triisopropylbenzene over different samples was tested in a home-made pulse microreactor based on a HP 4890D GC system. 50 mg of the catalyst (40–60 mesh) was pretreated under a high purity nitrogen flow at 400 °C for 1 h. 0.1 μl of 1,3,5-triisopropylbenzene was pulse-injected and carried by high pure nitrogen at a flow rate of 20 ml/min into the catalyst layer at 400 °C. The cracking products were separated using a HP-5 capillary column (length: 15 m, inner diameter: 0.530 mm, thickness of liquid film: 1.50 μm) with a programmed-temperature process from 40 to 200 °C and detected by an FID detector at 250 °C.

## 2 Results and discussion

### 2.1 Particle size distribution of MFI zeolite precursor sol

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