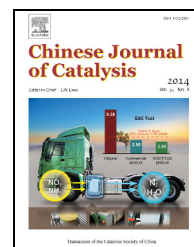


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Article

Synthesis of novel hierarchical ZSM-5 monoliths and their application in trichloroethylene removal

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ABSTRACT

A self-supporting ZSM-5 monolith with a hierarchical porosity was prepared using polyurethane foam (PUF) as a structural template and a hydrothermal synthesis procedure. The synthesized monolith was characterized and investigated towards the adsorption and catalytic oxidation of trichloroethylene (TCE). Adsorption of TCE was studied gravimetrically and oxidation of TCE was studied using a vapor-phase down-flow reactor. Monolithic ZSM-5 displayed good sorption properties and completely oxidized TCE. Conversion levels of 50% and 90% were achieved at reduced temperatures (by ~50 °C) when compared with the conversion temperatures obtained from the powder counterparts. Besides the activity of the monolith towards TCE adsorption and oxidation, it was stable and enhanced diffusion, thereby reducing pressure drops to a great extent owing to its hierarchical porous nature.

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1. Introduction

Zeolites are an important class of materials that are widely used in industrial processes that include catalysis and adsorption, owing to their selective nature and tailorable acidic property. Zeolites are usually available as a very fine powder that can cause significant decline in pressure and diffusion issues when employed in catalysis and adsorption industrial processes [1]. To address this issue, they are generally diluted with binders and shaped as pellets. However, this type of modification often alters important zeolite properties, occasionally restricting molecular diffusion, and altering the acidity and micropore size and volume [1,2]. Hence, in an attempt to maintain zeolite properties, improve diffusion, and reduce pressure drop, supporting zeolites on macroscopic structures were examined recently and subsequently tested in various applications [3,4]. However, with a few exceptions [5], the literature

studies typically investigate macroscopic structural supports such as cordierite and β -SiC over which the zeolite is either grown or deposited [6,7]. This method affords low zeolite loading amounts and requires multiple hydrothermal reactions with seeding.

According to the IUPAC convention [8], pores are classified based on their width; namely, micropores (< 2 nm), mesopores (2–50 nm), and macropores (> 50 nm). Zeolitic materials are mainly microporous [9]. To improve access of molecules to the adsorption/catalytic sites, hierarchically porous zeolites, i.e., materials that feature multiple types of pores mentioned above, are preferred. Post-synthesis treatments can generate hierarchically porous zeolites through selective leaching of aluminum (dealumination) or silicon (desilication) from the framework. Dealumination has been carried out to improve the acid strength and increase the intracrystalline mesoporosity by removing the tetrahedrally coordinated aluminum by leaching,

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using either steam or acid [10]. The major disadvantage of such a process is the partial reduction of the crystalline nature of the zeolite, consequently reducing the catalytic activity. A more recent process adopted to create hierarchical porosity in zeolites is desilication. In this method, leaching of silicon is conducted in an aqueous alkaline solution [11]. Desilication is highly suitable for introducing intracrystalline mesopores in the zeolite crystals, leading to an improved molecular diffusion and thus providing easier access to the micropores via the mesopores. However, if the Si/Al ratio is excessively low, the excess aluminum will inhibit the removal of silicon and subsequent formation of mesoporosity. Other methods, such as the use of secondary mesoporous templates, termed as hard templating, have also been examined; carbon, aerogel, and mesoporous silica spheres have been investigated as templates. However, this process is usually expensive and time-consuming [12]. The synthesis of monolithic ZSM-5 zeolites was achieved using a dry-gel conversion method [13] and mesoporous glass [1,14]. Cationic polymers have also been successfully employed to produce hierarchically meso-microporous zeolites [15]. Various other strategies have been applied to obtain zeolites with a hierarchical porosity, as described in various reviews [11,16]. Nevertheless, few strategies address the simultaneous creation of hierarchical porosity and the monolithic structure.

To overcome some of the drawbacks mentioned above, we synthesized a self-supporting zeolite monolith with a hierarchical porosity i.e., a monolithic-shaped material that has both micro- and mesopores, via a bottom-up approach using a hard-templating procedure. Relatively cheap polyurethane foams were used as a structural template during the hydrothermal synthesis. The zeolite that was built on the foam was shaped according to the shape of the foam. Final removal of the polyurethane template foam that is partially decomposed during the zeolite synthesis was achieved by calcination, thereby affording the monolithic shape of the zeolite. The zeolite has inherent micropores; the template is responsible for the formation of meso- and macropores in the monolithic zeolites, and these larger pores facilitate diffusion of gases and reduce the extent of pressure drops [12,17].

In the present work, we discussed the synthesis of self-supporting ZSM-5 monolith, its adsorption capabilities for trichloroethylene (TCE), and catalytic activity towards the decomposition of TCE. According to a recent study on the quality of air in Europe, air pollution and the various components lead to a reduced life expectancy of 8.6 months per person. The associated losses in productivity and medical costs in 2009 were estimated between EUR 102 and 169 billion (Environmental European Agency, Every breath we take Improving air quality in Europe, Luxembourg, 2013). TCE was selected as an example of a chlorinated volatile organic compound (VOC) that is among the most widespread toxic pollutants. VOCs are typically used as organic solvents in industrial dry cleaning and degreasing.

2. Experimental

2.1. Preparation of polyurethane foam (PUF)

The foam template was prepared according to a method previously described [18]. Briefly, polymer 4,4-methylene bisphenyl diisocyanate (MDI, BASF) was added to a mixture of polyol (F-5521, Repsol YPF), water, silicone oil surfactant (B8232, Evonik Industries AG), and catalysts 1,4-diazabicyclo[2.2.2]octane (DABCO 33LV, Air Products) and dibutyltin dilaurate (Merck, > 97%). The resulting mixture was stirred for 20 s, after which the homogeneous gel was transferred to a container and allowed to stand for 10 min for polymerization (growth of PUF) to take place. The PUF was placed in an oven at 70 °C for 30 min to ensure complete polymerization. The obtained PUF was cut into cylindrical shapes with a diameter of 2.5 cm and height of 5 cm, and used as a shape-directing template.

2.2. Preparation of self-supporting ZSM-5 monolith

ZSM-5 zeolite was prepared using a hydrothermal synthesis method. A precursor gel was prepared by vigorous mixing of 29.9 mL water, 6.1 mL zeolite pore structure-directing template tetrapropylammonium hydroxide (TPAOH), 11.03 mL tetraethyl orthosilicate as silica source, and 1.95 mL sodium aluminate (1 mol/L) as aluminum source. The resulting mixture was stirred further for 4 h. The homogeneous gel was transferred to a Teflon-coated autoclave containing the monolith shape-directing template PUF. The PUF was squeezed several times to remove air trapped in the foam to allow the gel solution to impregnate the foam. The autoclave was sealed tightly and placed inside an oven at 120 °C for 48 h under air flow. The monolithic zeolite ZSM-5 was subsequently obtained. The lightweight monolith was washed repeatedly until the pH of the filtrate was neutral. The pale yellow monolith was then calcined at 550 °C for 4 h at a heating ramp of 10 °C/min to produce a pure white crystalline ZSM-5 monolith.

2.3. Characterization

Powder X-ray diffractograms (XRD) were recorded on a Philips PX 1820 X-ray diffractometer using Cu K α source with a wavelength of 1.54 Å, operating at 20 mA and 50 kV. Scanning electron microscopy (SEM) images were obtained on a scanning electron microscope (Hitachi S2400) equipped with a standard energy-dispersive X-ray detector (EDS, Rontec). The open-cell volume and density of the PUF template and ZSM-5 monolith were measured with an automatic gas pycnometer (AccuPyc1330, Micrometrics) using dry nitrogen. The instrument chamber was purged 10 times at 170 kPa, then 10 expansion measurements were conducted at 170 kPa with an equilibrium criterion of 0.0345 kPa/min. The open-cell content was calculated from the external geometrical volume of a cylinder (V_e) (either polyurethane or ZSM-5 monolith) and the volume of the cylinder measured by gas pycnometry (V_g). The percentage fraction of the open volume, also known as the open-cell content, was calculated as follows: $(V_e - V_g)/V_e \times 100\%$. N₂ adsorption isotherms at -196 °C were measured on a Quantachrome (NOVA 2200e); ~0.05 g of the crushed monolith was degassed at 300 °C for 3 h prior to measurement.

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