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Short Communication

A facile route to synthesize mesoporous ZSM-5 zeolite incorporating high ZnO loading in mesopores

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ABSTRACT

Mesoporous ZSM-5 zeolite incorporating ZnO in mesopores has been synthesized with a simple route. The commercial H-ZSM-5 (Si/Al = 50) was first treated with NaOH solution to induce a partial desilication, which can introduce a large number of intracrystal mesopores, and the ZnO nanoparticles were successfully incorporated in the mesopores with wet impregnation method. Characterizations of XRD, UV–visible absorption spectra, TEM and N_2 adsorption were taken to analyze the locations of ZnO nanoparticles. The mesopores can load more than 15% ZnO with the size of about 20 nm, which can only reduce the mesopore surface area and volume, whereas, micropores are remained and cannot be blocked by the loaded ZnO particles.

1. Introduction

In recent years, semiconductor zinc oxide (ZnO) has attracted much attention due to its wide application such as varistors, gas sensors, solar cells, electrical and optical devices and catalysts [1]. When the particle size of ZnO decreases to nanometer or sub-nanometer scales, the quantum-size effects can be observed, which presents different electrical and optical properties from bulky ZnO [2]. Nowadays, many synthesis routes have been developed to control the size and distribution of semiconductor nanoparticles [3], whereas, the aggregation of nanoparticles is usually unavoidable, and the nanowires, nanorods and nanobelts of ZnO are prepared in difficulty. It is well known that incorporating nanoparticles inside the porous matrix can restrict further growth of the particles, which is an effective way to get monodispersed nanoparticles [4–7].

Zeolite is a kind of crystalline alumino-silicates composed of a great many micropores with uniform open windows in the framework, which can be extensively used as adsorbent and heterogeneous catalyst in industry [8]. In particular, faujasite (X and Y zeolite) with pore size of 0.74 nm is efficient to stabilize nanosized metal or metal-oxide particles with high dispersion in the interconnected channels [5,6a]. ZnO loaded HZSM-5 was proved to be a promising catalyst for the dehydrogenation of propane to propene in the presence of CO_2 if the acidity of the HZSM-5 support is decreased [6b]. The quantum size effect of nanoparticles in zeolite channels is obvious, but the incorporating loading is relatively low due to the pore size lower than 1 nm, thereby, most of the micropores or channels in zeolite are blocked by the incorporating materials. In recent years, mesoporous silica materials, such as MCM-41 and SBA-15 with the adjustable pore size (1.5–30 nm) and tailorable interior surfaces, are used as hosts to load metal oxides [4,7], which can disperse highly in the unblocked mesopores. It is well known that the mesoporous materials are generally composed of amorphous silica with very weak acidity, and the thermal stability and hydrothermal stability are lower than that of zeolites, which greatly restrict the further applications of mesoporous materials as well as the metal–oxide-loaded mesoporous materials as catalysts [9].

In past decades much attention has been put on the synthesis of mesoporous zeolites [10], which can effectively reduce the diffusion path of reactants and products in the zeolite phase. Generally, several strategies for the introduction of mesoporosity can be distinguished, including (i) soft templates in the form of surfactants or polymers, (ii) hard templates such as carbon- or resin-beads, or (iii) preformed biotemplates acting as scaffolds during synthesis, which are finally removed by subsequent calcinations to leave their mesoporous imprint [11]. Several post-synthesis techniques have been established to create extra mesopores in zeolite crystals, such as post-treatments of acid leaching [12] or base leaching [13]. For high silica zeolites (Si/Al > 5), alkaline treatment-induced desilication is powerful for creating extra mesopores, and the Al

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content suitable for mesopore formation is reported to be in the Si/Al ratio range of 20–50 for ZSM-5 zeolite [14]. Wu and co-workers have introduced mesopores into MOR crystals to improve the accessibility to Ti active sites, and a novel Ti-Meso-MOR has been made through the post-synthesis route, which exhibited an improved catalytic activity in the hydroxylation of toluene and the ammoximation of cyclohexanone as well [15]. The introduced mesopores could minimize the diffusion limitation and suppress coke formation efficiently [15]. Recently the mesoporous zeolite by desilication method has first been used as catalyst supports to load ruthenium for FT (Fischer–Tropsch) synthesis, in which the hierarchical porous structure and the unique acidity of the meso-ZSM-5 both play important roles in enhancing the selectivity to C_5–C_{11} and decreasing that to light hydrocarbons (CH_4 and C_2–C_4 alkanes) [16]. But the paper has not given the exact position of loaded Ru and adsorption properties of the Ru/meso-ZSM-5.

The novel mesoporous zeolites prepared by the simple desilication method can keep the self properties of zeolite with some interconnected mesopores produced by alkaline treatment as well [13]. The occurrence of mesopores in the single zeolite microcrystal gives us an opportunity to load high-content of metal oxides in zeolites with the micropore unblocked. Herein, we report a facile route for the first time to incorporate high ZnO loading (>15%) in mesoporous ZSM-5 zeolite by wet impregnation method (as shown in Scheme 1), which could be used as a kind of aromatization catalyst for the transformation of alcohols and alkanes to aromatics [6b,17].

2. Experimental

2.1. Synthesis of mesoporous ZSM-5

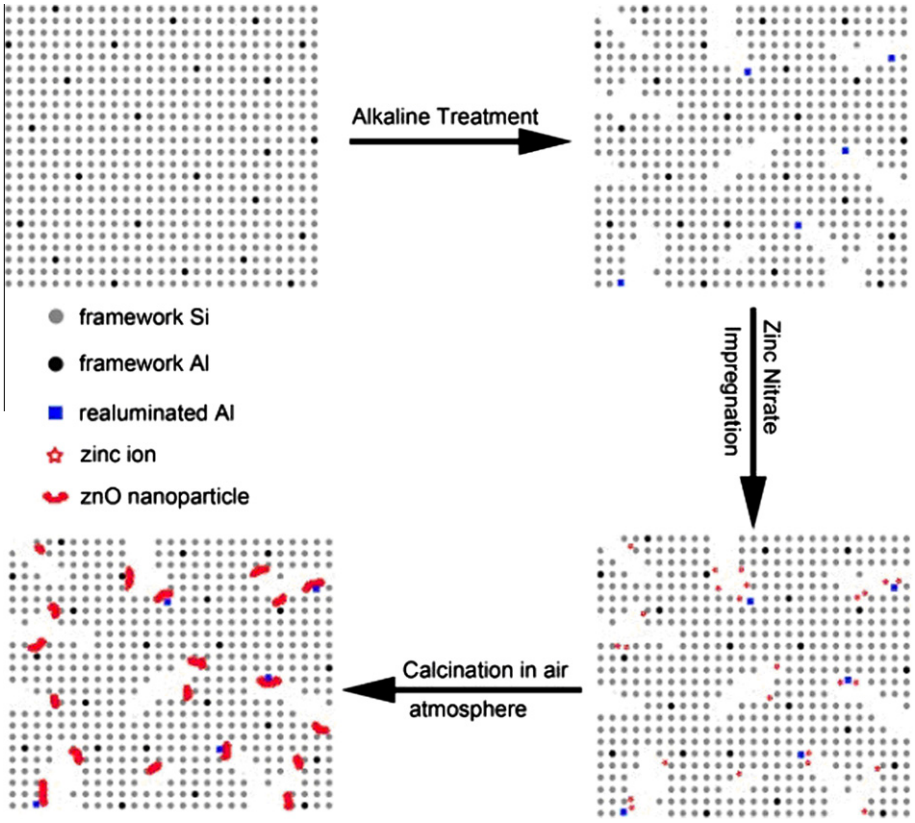
The parent zeolite used in this work was a commercial H-ZSM-5 (denoted as HZ) with a nominal Si/Al ratio of 50. Three grams of parent zeolite was treated with 90 g of 0.2 M NaOH aqueous solution for 70 min at 70 °C under stirring conditions. Subsequently the sample was washed intensively to remove the excess Na^+ ions, and filtered before being dried at 90 °C overnight, then the sample of mesoporous ZSM-5 (denoted as HZOH) was obtained.

2.2. Incorporation of ZnO in mesopores

The incorporation of ZnO was performed by impregnation of 1.0 g ZSM-5 zeolite into 10 g of a $Zn(NO_3)_2$ aqueous solution with different concentrations at 90 °C over 3 h under stirring conditions, which was then slowly dried at 60 °C for 6 h under stirring conditions. The powder was calcined in air at 550 °C for 5 h, and the sample was labeled as HZ*x*ZnO, in which *x* represents the mass ratio of ZnO to zeolite powder.

2.3. Characterizations

XRD identification was carried out with a Rigaku D-MAX/IIA X-ray diffractometer in a scanning range of 5–60° (2θ) at a rate of 4° (2θ)/min with Cu K_α radiation, 30 kV/20 mA. The surface area and pore volume were measured from the adsorption and desorption isotherms of N_2 at −196 °C using a Micromeritic Tristar 3000 instrument. UV–visible absorption spectra were obtained with a Shimadzu UV-2045 PC at room temperature. The size and morphology of samples were observed on a Philips XL30 SEM with accelerating voltage of 20 kV. TEM images were taken on a Jeol JEM-2010 TEM instrument with accelerating voltage of 200 kV to investigate the fine structure, morphology and particle size. The Si/Al ratio and content of ZnO in the zeolite were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Model ICPE9000 Shimadzu, Japan).



Scheme 1. Schematic representation of ZnO loading in the mesopores of alkali-treated zeolite.