



Short communication

Cu-ZSM-5 zeolite supported on SiC monolith with enhanced catalytic activity for NH₃-SCRQing Yuan^{a,b}, Zhenyi Zhang^{a,*}, Naisen Yu^a, Bin Dong^{a,*}^a Key Laboratory of New Energy and Rare Earth Resource Utilization of State Ethnic Affairs Commission, Key Laboratory of Photosensitive Materials & Devices of Liaoning Province, School of Physics and Materials Engineering, Dalian Minzu University, 18 Liaohe West Road, Dalian 116600, PR China^b State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China

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ABSTRACT

Here, we developed a new kind of hetero-structural catalyst through the homogeneous growth of Cu-ZSM-5 zeolite onto silicon carbide (SiC) monolith by using a one-pot hydrothermal method combined with an ion-exchange process in a rotary oven. The new catalyst formulation was tested towards NH₃-SCR, where the catalytic activity and stability of Cu-ZSM-5/SiC at T > 350 °C appear significantly higher than those obtained with Cu-ZSM-5 alone. In particular, the NO consumption rate of the former is 7.5 times larger on the average than that of the latter. This remarkable enhancement of catalytic activity is ascribed to the very good thermal conductivity of the SiC monolithic support. This research work could provide the means for the future design of more active and stable monolithic Cu-ZSM5-based catalytic systems with even lower Cu loading than the ones used in present de-NO_x applications.

1. Introduction

Nitric oxide emitted from the automotive vehicle is one of the most main atmospheric pollutants, posing ever-growing threats to the human health, ecological balance, and to social development. Eliminating nitrogen oxide effectively has always been the focus of researchers for years. After decades of exploration, ammonia assisted selective catalytic reduction (NH₃-SCR) has been regarded as an effective and widely-applied technology for DeNO_x [1–3]. In this area, V₂O₅-WO₃/TiO₂, ZSM-5, β and SSZ-13 are representative catalysts [4–7]. Among them, Cu-ZSM-5 appears to be one of the most promising zeolites for NH₃-SCR, mainly owing to its excellent deNO_x activity and the suitable temperature window of operation for light duty diesel engine exhaust gas streams, typically in the range 150–350 °C [8]. However, this catalytic system has the drawback of poor stability at high operating temperatures during the vehicle exhaust gas treatment [9,10]. Furthermore, from the viewpoint of a practical application, the powdery molecular sieves usually coated on ceramic supports do not meet the requirements of a good mechanical strength and high mass transfer rates. Thus, it is necessary to couple high-performance molecular sieves with proper support to construct a hetero-structural monolithic catalyst. To date, Cu-ZSM-5 has been coated on different kinds of ceramic materials in order to improve catalytic activity and stability of the low-temperature NH₃-SCR reaction [11]. Nevertheless, the realization of

good *high-temperature* activity for NH₃-SCR is a big challenge for the Cu-ZSM-5-based monolithic catalysts.

As it is well known, SiC with high thermal conductivity can transfer the local heat flux faster thus minimizing the deactivation of catalyst from overheating. This property might turn out to be helpful in improving the activity and stability of Cu-ZSM-5 at the high temperature range of the DeNO_x process. ZSM-5-coated SiC has been investigated in the catalytic reactions of methanol-to-propylene (MTP) [12] and methanol dehydration to dimethyl ether [13]. However, there is no report on the fabrication of a Cu-ZSM-5/SiC hetero-structural monolithic catalyst for the NH₃-SCR application to the best of our knowledge. In this work, the hydrothermal method was employed to uniformly grow the ZSM-5 solid structure onto the surface of SiC monolith in a rotary oven, and the effect of synthesis conditions on the growth of molecular sieves were investigated to some extent. After ion exchange of Cu²⁺, the Cu-ZSM-5/SiC catalyst obtained exhibits good catalytic activity (~50–60% NO conversion) and stability for the NH₃-SCR at the high operating temperature of the application.

2. Experimental

2.1. Preparation of pure ZSM-5

ZSM-5 was synthesized through a hydrothermal process. Typically,

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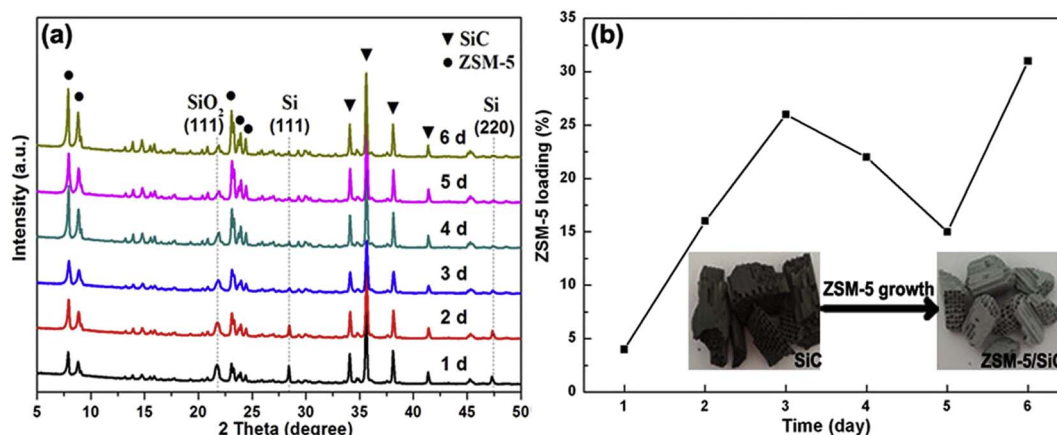


Fig. 1. Crystal phases (a) and the loading (wt%) of ZSM-5 deposited on SiC (b) during different synthesis reaction time.

8.52 g ethanol is added to 50 mL H₂O, followed by the addition of 11.278 g tetrapropylammonium hydroxide (TPAOH). After stirring for 30 min, 0.059 g Al₂O₃ and 9.63 g tetraethoxysilane (TEOS) are added to the mixture. Then, the resulting suspension is transferred into a Teflon-lined stainless-steel autoclave with a capacity of 50 mL. The autoclave is sealed and kept at 180 °C for 2 days and subsequently cooled to room temperature. The white powder is washed with ethanol and deionized water three times, respectively, followed by filtration and drying in air at 60 °C overnight. It is finally calcined at 550 °C for 5 h.

2.2. Preparation of ZSM-5/SiC composite

ZSM-5 was grown on a SiC monolithic support (67 wt% SiC, 18 wt% Si and 15 wt% SiO₂ with ca. 75 cells per square inch provided by BASF company) using the hydrothermal synthesis method. First, the mother liquor is prepared following the same procedure as that for the unsupported ZSM-5. Next, an appropriate amount of NaOH was added to adjust the pH value to ~14.1. Then, SiC is cut into small pieces and placed into the mother liquor in an autoclave of 50 mL. After reaction at 180 °C in a rotary oven (0.7 r/min, growth of ZSM-5 onto SiC support becomes more uniform) for a varying period of time, the composite is collected and ultrasonically washed with deionized water in a beaker and dried in air at 100 °C overnight. A ZSM-5/SiC composite is finally obtained following calcination at 550 °C for 5 h.

2.3. Preparation of Cu-ZSM-5/SiC composite

Cu-ZSM-5/SiC composite was subjected to an ion-exchange process using 0.5 mol/L Cu(NO₃)₂ aqueous solution at 80 °C for different duration, then washed with deionized water several times, and finally calcined at 550 °C for 5 h.

2.4. Catalyst characterization

Powder X-ray diffraction (XRD) is performed on a Panalytical X'pert Empyrean-100 diffractometer using a Cu K α source ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 40 mA. The XRD patterns are recorded in the range of $2\theta = 5^\circ \sim 50^\circ$ using a step of $0.19^\circ/\text{per sec}$. Scanning electron microscopy (SEM) measurements were conducted on a FEI Quanta 200 F microscope. The Cu loading in the ZSM5 zeolite was measured on a PerkinElmer 7300 DV inductively coupled plasma optical emission spectrometer (ICP-OES). The thermal conductivity measurements were performed by using a Transient Hot Disk TPS 2500S apparatus equipped with a 7577 probe (2.001 mm in radius) having a maximum uncertainty ($k = 2$) lower than $\pm 5.0\%$ of the reading. The specific surface area (SSA, $\text{m}^2 \text{g}^{-1}$) and pore structure (pore volume, mean pore size) of the ZSM-5 zeolite coating was determined by nitrogen (N₂)

adsorption–desorption isotherm measurements at 77 K using a Micromeritics ASAP2020 surface area and porosity analyzer (Quantachrome, American).

2.5. Catalytic performance

The catalyst sample with a powder particle size of 40–60 mesh was loaded into a fixed-bed microreactor made of quartz with an inner diameter of 6 mm, in which the catalyst bed height was 1.1 cm and the gas hourly space velocity (GHSV) was $80,000 \text{ h}^{-1}$. The NH₃-SCR was carried out under the inlet gas conditions: 500 ppm NH₃, 500 ppm NO, 10 vol% O₂, balance N₂, and 400 NmL/min total gas flow rate. The concentration of NO in the effluent gas stream was measured using an ECOTCH ML9841AS gas analyzer after appropriate calibration. The NO conversion was calculated according to the following relationship (Eq. 1):

$$\text{NO conversion (\%)} = \frac{C_{\text{NO}}^{\text{in}} - C_{\text{NO}}^{\text{out}}}{C_{\text{NO}}^{\text{in}}} \times 100\% \quad (1)$$

3. Results and discussion

3.1. Characterization of the ZSM-5/SiC composites

ZSM-5 was successfully grown on SiC support by the hydrothermal method under alkaline (use of NaOH) and *oven rotation* conditions. In order to control the thickness of ZSM-5 layer formed, the effect of growth time was studied. Fig. 1 shows the influence of time on growth (d, days) of the ZSM-5 onto the SiC support. As the time increases (Fig. 1a), the diffraction peaks of ZSM-5 become stronger and no impurity appeared (it appears only in the first 2 days on growth, Fig. 1a). With the impurity present in the SiC monolith, the peak at 21.6° is indexed as the cubic SiO₂ (111) planes (PDF#27–0605), and the diffraction peaks at 28.4° and 47.3° due to the cubic Si (111) and (220) planes (PDF#27–1402) become weaker or disappear completely, indicating that SiO₂ and Si have been consumed as Si source during the growth of ZSM-5. The photos of Fig. 1b show that after the growth of ZSM-5, the original SiC monoliths of black colour are covered with a uniform white layer. The sample was rubbed on a paper, and no white powder was fallen, indicating that a combination of chemical bonds between ZSM-5 and SiC, not a simple physical attachment, does exist.

The loading of ZSM-5 on SiC corresponding to different growth time was calculated and results are presented in Fig. 1b. During the period 1–3 days, the loading of ZSM-5 increases linearly from 4% to 26%. Three days later, the loading declines to some extent until the fifth day. This may be due to the fact that the interaction between the grown ZSM-5 grains in the outermost layer reaches a limit after 3 days. When

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