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Article

Growth of Cu/SSZ-13 on SiC for selective catalytic reduction of NO with NH_3

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ABSTRACT

Silicon carbide (SiC) was used as a support for SSZ-13 zeolite in an attempt to improve the high-temperature stability and activity of Cu/SSZ-13 in the selective catalytic reduction (SCR) of NO with NH_3. SSZ-13 was grown via a hydrothermal method using the silicon and silica contained in SiC as the source of silicon, which led to the formation of a chemically bonded SSZ-13 layer on SiC. Characterization using X-ray diffraction, scanning electron microscopy, and N_2 adsorption-desorption isotherms revealed that the alkali content strongly affected the purity of zeolite and the crystallization time affected the coverage and crystallinity of the zeolite layer. Upon ion exchange, the resulting Cu/SSZ-13@SiC catalyst exhibited enhanced activity in NH_3-SCR in the high-temperature region compared with the unsupported Cu/SSZ-13. Thus, the application temperature was extended with the use of SiC as the support.

1. Introduction

Nitrogen oxides (NO_x) emitted from vehicles are a major contribution to air pollution because of their toxicity. Selective catalytic reduction (SCR) with NH_3 is regarded as one of the most efficient approaches to remove NO_x, transforming them into non-toxic N_2 and H_2O. This approach is widely applied as a denitration ($DeNO_x$) process [1–3]. Various catalysts have been developed and tested [4–6]. For example, vanadium–tungsten–titania-based catalysts have been commercially used for more than three decades [7,8]. However, these catalysts fail to convert NO_x under lean-burn conditions with high air/fuel ratios.

Zeolites have also been widely studied for SCR with NH_3, including ZSM-5 with the MFI structure, beta zeolite, SAPO-34, and SSZ-13 with the CHA structure [9–11]. The Cu (or Fe) ion-exchanged ZSM-5 exhibited better performance than a commercial vanadia–titania catalyst [12,13]. However, their stability remains an issue because of the sintering of copper species and disruption of zeolitic crystallinity and porosity under harsh reaction conditions [14,15]. In comparison, Cu/Fe ion-exchanged beta catalysts exhibited better durability [1,16]. CHA-

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type zeolite with smaller pores and stronger acidity, especially SSZ-13 zeolite upon exchange with Cu^{2+}, has been shown with better NH_3-SCR activity and selectivity than those of beta catalysts and ZSM-5 as well as higher hydrothermal stability [17–22]. However, these zeolite-based catalysts still undergo deactivation above 550 °C. In real applications, the temperature can reach beyond 800 °C, which frequently degrades the durability of the catalyst. Therefore, it is desirable to develop catalysts which can be applied at a wider temperature window beyond 550 °C or even higher.

Silicon carbide (SiC) is a chemically inert and mechanically stable material with a thermal conductivity that is two orders of magnitude higher than that of SiO_2 and three times higher than that of alumina [23–25]. With these interesting properties, we explore the use of SiC as the support for a zeolite-based SCR catalyst in an attempt to strengthen its anti-thermal shock and improve its high-temperature stability. Gu et al. [23] reported that a Mo-ZSM-5/porous SiC catalyst exhibited clearly improved activity in the methane dehydroaromatization reaction. In addition, Elamin and coworkers [24] reported that a SAPO-34/SiC composite with a foam structure exhibited excellent selectivity and stability in methanol dehydration to a dimethyl ether. In this study, we demonstrate that SSZ-13 can be grown directly on the surface of SiC using a hydrothermal method, as confirmed by powder X-raydiffraction (XRD), scanning electron microscopy (SEM), and nitrogen adsorption–desorption results. The use of the SiC support enhances the catalytic activity of Cu/SSZ in the NH_3-SCR reaction compared with that of unsupported Cu/SSZ-13.

2. Experimental

2.1. Chemicals

NaOH, *N*,*N*,*N*-trimethyl-1-ammonium adamantane (TMAdaOH), $Al(OH)_3$, and fine SiO_2 powder were purchased from Sinopharm Chemical Reagent Co., Ltd., InnoCHEM, Tianjin Kemel Chemical Reagent Co., Ltd., and Shenyang Chemical Industry Co., Ltd., respectively. All the chemicals were directly used as received without further purification.

2.2. Preparation

2.2.1. Preparation of pure SSZ-13

The pure SSZ-13 was synthesized using a hydrothermal method adapted from that reported by Shishkin et al. [26]. Typically, 4 g H_2O was added to 3 g NaOH aqueous solution (1 mol/L), followed by the addition of 4 g TMAdaOH. After stirring for 30 min, 0.1 g $Al(OH)_3$ and 1.2 g SiO_2 were added to the mixture. The resulting suspension was then transferred into a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed and maintained at 160 °C for 2 d in a rotary oven (0.7 r/min) and subsequently cooled to room temperature. The resulting white powder was washed with ethanol and deionized water three times, sequentially, using filtration, followed by drying in air at 100 °C overnight. Finally, the powder was calcined for 5 h at 550 °C.

2.2.2. Preparation of SSZ-13@SiC

SiC samples were provided by BASF. The SSZ-13 was grown on SiC using a hydrothermal synthesis method. First, the mother liquor was prepared following the same procedure as that for the unsupported SSZ-13. Then, SiC with dimensions of 0.5 cm × 0.5 cm × 1 cm was added into the mother liquor in an autoclave with a capacity of 50 mL. After reaction at 160 °C in a rotary oven (0.7 r/min) for varying periods, the composites were collected and ultrasonically washed with deionized water in a beaker and dried in air at 100 °C overnight. SSZ-13@SiC was finally obtained following calcination for 5 h at 550 °C.

2.2.3. Preparation of Cu/SSZ-13@SiC

The SSZ-13@SiC was subjected to ion exchange using 0.5 mol/L $Cu(NO_3)_2$ aqueous solution at 80 °C for different durations, followed by calcination for 5 h at 550 °C. The resulting catalyst was named Cu(*X*)/SSZ-13@SiC, where *X* represents the Cu loading (in mass percentage). For comparison, unsupported Cu/SSZ-13 was also prepared following the same method.

2.3. Characterization

Powder XRD was performed on a Panalytical X'Pert Empyrean-100 diffractometer using a Cu K_α source (λ = 1.5418 Å) at 40 kV and 40 mA. The patterns were recorded in the range of 2θ = 5°–50° using a step of 0.19°/s. SEM was performed on a FEI Quanta 200 F microscope. The Cu loadings were measured using inductively coupled plasma optical emission spectrometry (ICP-OES; PerkinElmer 7300 DV). N_2 adsorption–desorption isotherms were measured at −196 °C using a Quantachrome QUADRASORB SI system. The specific surface areas of the samples were calculated using the Brunauer-Emmett-Teller (BET) equation.

2.4. NH_3-SCR activity measurements

The catalyst (0.18 g) with a size of 40–60 mesh was loaded into a fixed-bed microreactor made of quartz with an inner diameter of 6 mm. The reaction was performed under the following conditions: 500 ppm NH_3, 500 ppm NO, 10 vol% O_2, 5 vol% H_2O, balance N_2, 400 mL/min total gas flow, and 80000 h^{-1} gas hourly space velocity (GHSV). The concentration of NO in the effluent was analyzed using an ECOTCH ML9841AS analyzer. The NO conversion was calculated using the following equation: NO conversion = $(C_{NO,in} - C_{NO,out})/C_{NO,in} \times 100\%$.

3. Results and discussion

3.1. Structure of SSZ-13@SiC composites

Fig. 1 presents XRD patterns of the SiC support, pure SSZ-13, and SSZ-13@SiC. The XRD pattern for the SiC support (Fig. 1(a)) contains typical diffraction peaks for hexagonal SiC at 34.1°, 35.6°, 38.1°, and 41.4° corresponding to the (101), (006), (103), and (104) planes (PDF #49-1428), respectively. In addition, the peak at 21.6° is attributed to cubic SiO_2 (111) (PDF #27-0605), and those at 28.4° and 47.3° are indexed as the