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Short communication

Size controlled ZSM-5 on the structure and performance of Fe catalyst in the selective catalytic reduction of NO_x with NH_3

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ABSTRACT

Fe/ZSM-5 catalysts with various morphologies and sizes were prepared and the catalytic properties in NH_3-SCR were also investigated. The different ZSM-5 morphologies and sizes indeed influence the dispersion of Fe species. The Fe/ZSM-5 catalyst, which was cauliflower-like morphology of ZSM-5 support aggregated by small nanocrystal zeolite with crystallite size of about 50 nm, exhibited the best NH_3-SCR activity ($T_{\geq 90\%}$ = 280–650 °C). This specific morphology and size of ZSM-5 support were considered to benefit the distribution of isolated Fe^{3+} species, which was proved to be the main active sites in SCR reaction.

1. Introduction

NO_x ($x = 1, 2$), one of the significant pollutants in the atmosphere, can result in a series of environmental issues, such as acid rain, photochemical smog, ozone depletion and so on [1]. Selective catalytic reduction (SCR) of NO_x with NH_3 is presently considered as one of the most efficient methods for the abatement of NO_x. Currently, the V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2 are the most widely used catalysts in a relatively narrow temperature window of 300–400 °C that can achieve the acceptable efficiency, but this system has some problems, such as the volatility and toxicity of vanadium species, low N_2 selectivity at high temperatures and high conversion of SO_2 to SO_3 [2,3].

To overcome these defects and develop new SCR catalysts, many transitional metals, transitional metal oxides and zeolite catalysts [4,5] have been studied in the past decades. Among them, Cu and Fe are deemed the most promising SCR catalysts [6], especially iron-based zeolites, which has been shown to produce less amounts of N_2O and to be less sensitive to water than copper-based zeolites [7]. Much research has been devoted to Fe-based zeolites, such as Fe/ZSM-5, Fe/MOR, Fe/MFI and Fe/β [8–11]. In particular, Fe/ZSM-5 is subject to more attention for its nontoxicity, better hydrothermal stability and high activity at high temperature (>300 °C) [6,12]. Iwasaki et al. [13] researched effects of Si/Al ratios on NH_3-SCR activity and found that the catalytic activity decreased with increasing Si/Al ratios. Moreover, his research group [14] made a survey that different preparation method such as impregnation, reductive solid-state ion exchange and chemical vapor deposition had a strong effect on NH_3-SCR activity in the Fe/ZSM-5 catalysts. Schwidder et al. [15] investigated the relation of the activities with the concentration of different Fe sites in Fe/ZSM-5 catalysts. Grümert et al. [16] further confirmed that the different Fe sites worked in standard and fast NH_3-SCR over Fe/ZSM-5 catalysts. Besides, Kröcher et al. also surveyed the impact of hydrothermal deactivation of Fe/ZSM-5 catalysts on the NH_3-SCR in the 10% H_2O, finding that catalyst deactivation was owing to the detachment of Fe^{3+} from ion exchange positions, which leads to the formation of FeO_x clusters and the remaining activity in aged catalysts was attributed to unaffected isolated iron sites [17].

However, studies of the effect of morphology and the size of ZSM-5 on the SCR activity are quite rare. To improve the applicability of this Fe/ZSM-5 catalyst, it is necessary to investigate these effects for the Fe/ZSM-5 catalyst. In this paper, three Fe/ZSM-5 catalysts were studied and they showed excellent activities in SCR reaction. Both of the different morphologies and sizes of ZSM-5 catalyst, which influenced the distribution state of Fe species, finally were related to NH_3-SCR performance.

2. Experimental

2.1. Catalyst preparation

Three types of ZSM-5 with the same Si/Al (SiO_2/Al_2O_3 = 100) were prepared according to relative references [18–21] and Fe/ZSM-5 catalysts were prepared by wet impregnation method (shown in the

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Supplementary material). Three Fe/ZSM-5 catalysts are abbreviated to FeZ1, FeZ2 and FeZ3, respectively.

2.2. Catalytic characterization

The N_2 adsorption–desorption isotherms were performed using a Surface Area and Porosity Analyzer (ASAP2020-M). The specific surface area were calculated by the BET (Brunauer–Emmett–Teller) method. Powder XRD measurements were carried out on a Bruker AXS-D8 Advance powder diffractometer with a Cu Kα radiation source of wavelength of 1.5406 Å. SEM images were recorded with Hitachi S-4800. The samples were dispersed into alcohol and then coated with gold to improve conductivity before observation. TEM images were recorded with Tecnai G2 F20. The samples were dispersed into alcohol before observation. H_2-TPR experiments were performed with a Micromeritics AutoChem II Chemisorption Analyzer equipped with a thermal conductivity detector (TCD). The XPS was measured using Kratos Axis Ultra DLD spectrometer equipped with an Al Kα radiation (1486.6 eV) (Thermo VG Corporation, USA). The binding energy calibration was checked by the line position of C1s as an internal reference (284.6 eV). UV–vis measurements were recorded with a Hitachi U-4100 (Japan) at room temperature in a wavelength region between 200 and 800 nm. The absorption spectra were converted to the Kubelka–Munk function defined by $F(R) = (1 - R)^2 / (2R)$, where R is the reflectance.

2.3. Activity tests

The NH_3-SCR reaction activities were performed by using MRU Air fair emission monitoring systems (VARIO PLUS). The typical reactant gas composition was as follows: 500 ppm NO_x, 500 ppm NH_3, 5% O_2, He balance. The total flow rate of the reaction mixture was 300 mL/min (gas hourly space velocities (GHSV): 108,000 h^{-1}). Experimental diagram containing reaction equipment is shown in the Supplementary material.

3. Results and discussion

3.1. Catalytic activity

Fig. 1 shows the NO_x conversion as a function of reaction temperature ranging from 150 to 650 °C over Fe/ZSM-5 catalysts. It can be clearly seen that NO_x conversion displayed a marked increase below 350 °C. Further increasing the temperature to above 450 °C led to some decrease. Table 1 summarizes the reaction temperature $T_{\geq 90\%}$ (corresponding to the NO_x conversion ≥90%) of different catalysts. It could be found that the $T_{\geq 90\%}$ of FeZ1 catalyst was obtained from 280 to 650 °C. For FeZ2 and FeZ3 catalysts, the $T_{\geq 90\%}$ was 300–595 °C and 330–500 °C, respectively. Clearly, the FeZ1 catalyst exhibited the best low temperature activity and broadest operation temperature window. The FeZ3 catalyst was inferior to FeZ2 in catalytic performance at lower temperature and operation temperature window. Furthermore, excellent N_2 selectivity over all Fe/ZSM-5 catalysts could be obtained, at above 80% from 150 to 650 °C (inset, Fig. 1). Compared with a Fe/ZSM-5 catalyst which has been industrially and commercially used for NH_3-SCR, the operation temperature window of catalysts prepared in this study was more than 40 °C lower in the whole temperature range.

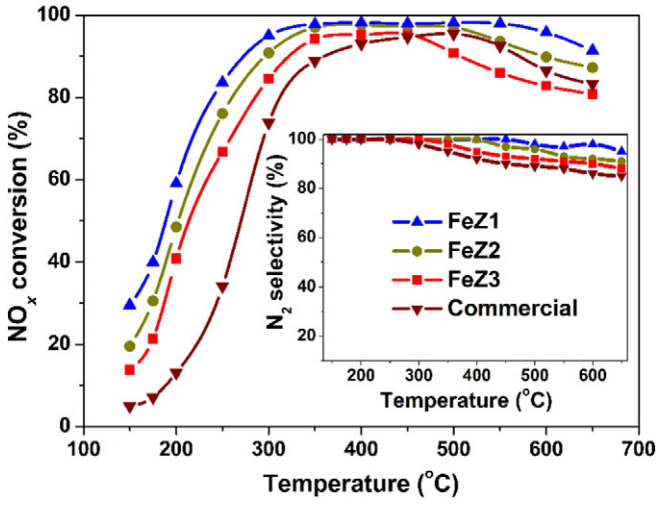

Fig. 1. NH_3-SCR activities of different catalysts.

3.2. Catalyst characterization

3.2.1. SEM and TEM results

All Fe/ZSM-5 catalysts exhibited the typical lines of MFI framework (Fig. S1 in the Supplementary material), indicating that the structure of the MFI remained intact even after Fe loading [22,23]. The BET surface areas of all Fe/ZSM-5 catalysts are provided in Table 1. All the catalysts prepared in this study (FeZ1, FeZ2 and FeZ3) showed higher surface area compared with that of commercial Fe/ZSM-5 catalyst. Fig. 2 exhibits the SEM and TEM images of different catalysts. It can be seen that there were distinct morphologies for different ZSM-5. Z1 has a relatively rough surface and presented a cauliflower-like morphology with crystallite size of 600 nm and was aggregated by small nanocrystal zeolite with crystallite size of about 50 nm. Z2 has also rough surface, but the morphology is irregular spherical with the zeolite particles size of 100–300 nm. Z3 has a smooth surface and showed the uniform spherical morphology with the nano-spherical size of about 200 nm. After the Fe was loaded into ZSM-5, the Fe species were observed by TEM, which were well distributed on the external surface of the ZSM-5. The Fe nanoparticles sizes of FeZ1, FeZ2 and FeZ3 were about 10, 15 and 20 nm, respectively. That was to say, the different morphology and particle size influenced the Fe species dispersion. The cauliflower-like morphology of ZSM-5 was able to induce better dispersion of Fe species. Specifically, the Fe nanoparticles on the external of cauliflower-like morphology and larger nanoparticle ZSM-5 showed the small particle size, finally resulted in higher NH_3-SCR activity. Consequently, ZSM-5 support was the key factor to achieve the better catalytic activity.

3.2.2. XPS results

Fig. S2 shows the XPS results of various Fe/ZSM-5 catalysts. The $Fe2p_{3/2}$ spectra could be separated into two peaks by the same peak fitting deconvolution at about 709.6 and 712.2 eV (Fig. S2a). It has been reported that Fe^{3+} are characterized by $Fe2p_{3/2}$ binding energies in the range of 711–712 eV [24]. Two distinct bands centered at about 710 eV and 712 eV were deconvolved, which is approximately close to the range of the $Fe2p_{3/2}$ binding energies of iron in Fe^{2+} and Fe^{3+}, respectively [25,26]. So it is suggested that Fe^{3+} and Fe^{2+} species were present on the surface of the samples. The relative surface contents of Fe^{2+} and Fe^{3+} for each sample were calculated and summarized in Table 1. The Fe^{3+}/Fe^{2+} molar ratio decreased in the order of FeZ1 > FeZ2 > FeZ3 in various Fe/ZSM-5 catalysts, which was in accordance with the sequences of catalytic performance in Fig. 1. That is to say, the Fe^{3+} species might be the active sites over Fe/ZSM-5 catalyst in NH_3-SCR. The curves of O1s spectra fitted into two peaks are shown in Fig. S2b. The peak at 530.2 eV was characteristic of lattice oxygen O^{2-} (denoted as O_α), and the one at 531.6 eV corresponds to the surface adsorbed oxygen (denoted as O_β) such as O_2^{2-} or O^- belonging to defect-oxide or hydroxyl-like group [27,28]. A quantitative analysis indicated that O_β/O_α molar ratio increased in the order of FeZ2 < FeZ3 < FeZ1 (Table 1), which was incompletely coinciding with the sequences of NH_3-SCR activity. This suggested that surface adsorbed oxygen played a role to some extent but not to be decisive in NH_3-SCR.