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Nanofibrous SUZ-4 loading Pt used for selective catalytic reduction of NO_x by hydrogen

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ABSTRACT

Nanofibrous SUZ-4 zeolite (NF) was synthesized for preparing the Pt/HSUZ-4 catalyst used in the selective catalytic reduction of NO_x by hydrogen (H_2-SCR). The seed dissolution during the crystallization played an important role for the nanofibrous SUZ-4 formation. It was found that the zeolite NF is oriented along the 10-ring channels, and it has much more Brönsted acid sites on its external surface compared with general SUZ-4 zeolite. Consequently, Pt primarily existed as the well-dispersed particles (~5 nm) on the NF external surface for the Pt/NF catalyst prepared by impregnation. In comparison with 0.1 wt.% Pt/HZSM-5 as well as general 0.1 wt.% Pt/HSUZ-4, the 0.1 wt.% Pt/NF catalyst gave much higher activity and N_2 selectivity in the H_2-SCR. For identifying the Pt ions in SUZ-4 zeolite channels, the band at 1652 cm^{-1} ascribed to nitrous species adsorbed on the ions was proposed.

1. Introduction

To meet strict emission regulation, effective elimination of NO_x has become one of the greatest challenges for the researchers in the environmental protection field [1,2]. Recently, selective catalytic reduction of NO_x by hydrogen (H_2-SCR) has been drawn much attention due to the low operation temperature (100–200 °C) [3–5]. It has been widely accepted that Pt is the most active metal for catalyzing the reaction, and its catalytic activity and the N_2 formation selectivity in the reaction are drastically influenced by the property of support [6,7]. For example, Satsuma and co-workers [8,9] have found that zeolite supported Pt catalyst was much more selective for NO_x reduction to N_2, compared with metal oxide supported Pt catalyst. They have proposed that the acid sites on the support should be involved in the NO_x reduction, via adsorbing the reactive species NH_4^+. Guan et al. [10] have also found that the activity of Pt/MCM-41 was significantly improved by incorporating Al into the MCM-41. Yu et al. [11] found that excess load of Pt on HZSM-35 (>1.0 wt.%) made strong acid sites on the zeolite largely lost, which is the reason why large amount of Pt loading on the zeolite leads to the activity decrease. High activity and N_2 selectivity were also achieved on the catalyst of Pt/HFER zeolite [12]. Clearly, the strong acid sites on support are necessary for the H_2-SCR over Pt catalysts. Hence, the higher activity and selectivity in the reaction can be expected over the catalyst of Pt being loaded on the support with stronger acidity and/or more acid sites.

SUZ-4 has been reported to possess large amount of Brönsted acids that are even stronger than those on HZSM-5 in acidity, after being exchanged by protons [13]. Just because of the strong acidity, the proton-form of SUZ-4 (HSUZ-4) exhibited considerably high catalytic activity in many reactions, such as the ethylene dimerization [14], *n*-butene isomerization [15], *n*-hexane cracking [16], and selective catalytic reduction of NO_x by ethylene in the presence of steam [17]. The abovementioned acidic property and the catalytic performance of HSUZ-4 as an acid catalyst encourage us to speculate that the zeolite would be a promising support loading Pt used in H_2-SCR. As expected, much higher activity and N_2 selectivity were given by the Pt/HSUZ-4 catalyst in comparison with Pt/HZSM-5 in our investigation.

On the other hand, a nanofibrous SUZ-4 zeolite was synthesized for loading Pt as the catalyst support in the reaction in this paper. In literature, zeolites in nanoscale with different shape have been synthesized, such as with nanoparticles [18], nanosheets [19,20] and nanofibers [21]. It has been reported that, for MFI zeolite nanosheets, with their thickness decreasing, the thermal stability of Pt particles on the zeolite considerably increases, which leads to dispersion of Pt on the zeolite becoming better [20]. In this paper, it was found that nanofibrous HSUZ-4 loading Pt is much more active and selective than general one loading Pt. We propose that the quite different dispersion of Pt particles on the zeolite outside surface, being associated with Brönsted acid sites on the external

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surface and the length of channels with maximum pore, is responsible for the activity results.

2. Experimental

2.1. The SUZ-4 zeolite synthesis and the catalyst preparation

The nanofibrous SUZ-4 zeolite was synthesized with assistance of seed slurry according to our previous report [22], in which organic template was not used. For the synthesis, 17 wt.% of seed slurry obtained by crystallizing the gel (7.9 KOH: Al_2O_3: 21.2 SiO_2: 2.6 TEAOH: 498.6 H_2O) at 150 °C for 16 h was added to an initial gel of 7.9 KOH: 1.0 Al_2O_3: 21.2 SiO_2: 498.6 H_2O with strong stirring. After an extra 30 min of stirring, the mixture was transferred to the autoclave and heated at 150 °C for certain time under the 20 rpm rotation. In one batch of the synthesis, always 0.2 g Al foil was used, irrespective of the seed slurry preparation or the zeolite synthesis. To track down the zeolite crystallization process, the phase evolution of the solid in the synthesis system was measured by XRD, SEM, and TEM as necessary. The corresponding solid samples were labeled with the crystallization time, e.g. 3 h. For comparison, the general SUZ-4 zeolite (rod-like) was synthesized according to literature [23], in which template was added instead of the seed slurry.

The two kinds of SUZ-4 with 100% relative crystallinity, being synthesized by 96 h crystallization, were used as parent zeolites. The proton-form zeolites were obtained by ion-exchanging the parent zeolites in NH_4NO_3 aqueous solution at 150 °C for 12 h, which were labeled as NF or ROD according to their morphology.

The catalysts of Pt/HSUZ-4 containing 0.1 wt% Pt were prepared by incipient wetness method, which were labeled as Pt/NF or Pt/ROD according to their supports. For comparison, Pt/HZSM-5 with the same Pt loading amount was also prepared by the method using the commercial HZSM-5 (with SiO_2/Al_2O_3 of 25, purchased from Nankai University) as support. For all the catalysts, H_2PtCl_6 was used as the Pt precursor.

2.2. Characterization

The XRD measurement was carried out using Cu Kα radiation at 30 kV and 30 mA and with a scan speed of $5^\circ\ \mathrm{min}^{-1}$. Relative crystallinity (*RC*) of the samples was calculated using the rod-like SUZ-4 zeolite (obtained at 96 h) as reference, based on the intensity of diffraction peak at $2\theta = 7.8^\circ$ in the formula (1):

$$\mathrm{RC}\ (\%) = \frac{\text{The peak intensity of the sample}}{\text{The peak intensity of the reference sample}} \times 100\% \quad (1)$$

Morphology of the samples was observed by field emission scanning electron microscopy (SEM) on QUNATA200 FEG. A small amount of Gold was deposited on the specified sample as the pretreatment of SEM observation. Transmission electron microscopy (TEM) was performed on FEI Tecnai F30 electron microscope. To identify the orientation of nanofibrous SUZ-4 zeolite, HR-TEM was conducted on TECNAI G^2 F30. For the TEM and HR-TEM observations, the suspensions of powder samples suspended in ethanol were dropped onto copper grids with holey carbon films.

X-ray fluorescence (XRF) was conducted on the spectrometer SRS 3400 (Bruker) to analyze the Si and Al contents of SUZ-4 zeolites. For the measurement, the samples were melted with $12LiBO_2 \cdot 22Li_2B_4O_7$.

FTIR was performed in a quartz IR cell equipped with CaF_2 windows on a Bruker TENSOR 27 FTIR Spectrophotometer at a resolution of $4\ \mathrm{cm}^{-1}$ for 32 scans, to characterize the hydroxide groups in the zeolites [24] as well as the surface species. The acid sites on the external surface of the zeolites were measured according to literature [25] using 2,6-dimethlpyridine as adsorbate. The nitric species on the Pt/HSUZ-4 catalysts and the supports were measured according to literature [12]. Prior to the measurements, self-supporting wafer of sample was pretreated in the flow of 20% O_2/N_2 or 1.3% H_2/N_2 at 500 °C for 30 min.

Temperature-programmed desorption of ammonia (NH_3-TPD) was conducted on a CHEMBET TPD/TPR analyzer (Quantachrome Instruments) to measure the total amount of acid sites on the zeolites. The samples (0.2 g) were pretreated in He at 700 °C for 30 min, exposed to the gas mixture of 6.6% NH_3/He for 1 h at 80 °C, and purged with He (100 ml/min) for 1 h. Then, the TPD signal was recorded by TCD in the He flow (100 ml/min) from 80 to 700 °C with a temperature ramp rate of 10 °C/min.

2.3. Catalytic test for H_2-SCR

The catalytic H_2-SCR reaction ($H_2 + NO + O_2 \xrightarrow{Cat} N_2 + N_2O + H_2O$) was carried out in a quartz reactor (i.d. 4 mm) at atmospheric pressure. Granular catalysts (20–40 meshes, 0.2 g) were fixed in the reactor and pretreated in the flow of 20% O_2/N_2 or 1.3% H_2/N_2 at 500 °C for 30 min prior to the activity measurement. The reactant gas mixture consisting of 1000 ppm NO_x, 5000 ppm H_2, 10% O_2 in N_2 was fed into the reactor with a total flow rate of 100 ml/min ($GHSV \approx 16{,}000\ \mathrm{h}^{-1}$) at the desired reaction temperatures in the range of 200–80 °C. H_2 was analyzed online by gas chromatograph (GC7890) filled with 13× molecular sieve column (i.d. 2.5 mm, length 3 m) being kept at 313 K using a TCD as detector. Nitrous oxide (N_2O) was analyzed online by gas chromatograph (GC7890) equipped with a column (i.d. 2 mm, length 35 cm) being filled with carbon unibeads kept at 313 K using TCD as detector. NO_x (NO and NO_2) were simultaneously analyzed by a chemiluminescence NO_x analyzer (Eco Physics, CLD62). For the catalysts, the NO_x conversion and N_2 selectivity were calculated by the formula (2) and (3), respectively:

$$NO_x\ \text{conv.}\ (\%) = \frac{c(NO_x)_{in} - c(NO_x)_{out}}{c(NO_x)_{in}} \times 100\% \quad (2)$$

$$S_{N_2}(\%) = \frac{c(NO_x)_{in} - c(NO_x)_{out} - 2c(N_2O)_{out}}{c(NO_x)_{in} - c(NO_x)_{out}} \times 100\% \quad (3)$$

In the equations, the $c(NO_x)_{in}$ and $c(NO_x)_{out}$ represent the total concentration of nitrogen oxide (NO and NO_2) in the inlet and outlet gas of the reactor, respectively. Similarly, $c(N_2O)_{out}$ denotes the N_2O concentration in the outlet gas. Since NO is partially oxidized to NO_2 in gas phase by O_2 at room temperature, both before reaching and after leaving the catalyst bed, the conversion of NO_x rather than that of NO was chosen to evaluate the H_2-SCR activity of catalyst.

3. Results and discussion

3.1. The SUZ-4 morphology determined by the crystallization process

The morphology of nanofibrous (∼12 × 1500 nm) and rod-like (∼100 × 750 nm) SUZ-4 zeolites is illustrated in Fig. 1. To figure out the crystallization processes of the two zeolites in their syntheses, several samples were taken out at different crystallization time for monitoring the phase evolution. The crystallization curves based on the XRD measurement are given in Fig. S1. At least 96 h was required for the 100% rod-like SUZ-4 zeolite formation, although the increase of *RC* given in formula (1) in the crystallization period of 12–16 h seemed to be quite drastic. However, it can be seen that, the 100% nanofibrous zeolite was obtained at the crystallization time of 65 h, although the crystallization in the early period of 0–16 h was slow and even the *RC* was significantly decreased in the early 3 h. The *RC* decrease should be originated from the partial dissolution of the crystals that were introduced by the seed slurry, which can be confirmed by the SEM and TEM