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Novel promoting effects of cerium on the activities of NO_x reduction by NH_3 over TiO_2-SiO_2-WO_3 monolith catalysts

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Abstract: A series of catalysts were prepared by doping different loadings of CeO_2 over TiO_2-SiO_2-WO_3 and used for the selective catalytic reduction of NO_x by NH_3. The experimental results showed that the selective catalytic reduction (SCR) performance and SO_2-resistant ability of TiO_2-SiO_2-WO_3 were greatly enhanced by the introduction of cerium. The catalyst containing 10% CeO_2 showed the highest NO conversion in a wide temperature range and good N_2 selectivity with broad operation temperature window at the gas hourly space velocity (GHSV) of 30000 h^{-1}, which was a very promising catalyst for NO_x abatement from diesel engine exhaust. The catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), N_2 adsorption-desorption (BET) and X-ray photoelectron spectroscopy (XPS). The characterization results showed that the bigger pore radius, higher surface atomic concentration and dispersion of Ce and the abundant adsorbed oxygen on the surface of catalyst contributed to the best NH_3-SCR performance of CeO_2/TiO_2-SiO_2-WO_3 catalyst containing 10% CeO_2.

Keywords: NH_3-SCR; NO; cerium; CeO_2/TiO_2-SiO_2-WO_3; monolith catalyst; rare earths

Nitrogen oxides (NO_x), which can lead to the formation of troposphere ozone, photochemical smog and acid rain, are becoming one of the major sources of air pollutions, and among all the methods applied for removing NO_x, NH_3-SCR is considered as one of the most favored techniques[1,2]. Commercial V_2O_5-WO_3/TiO_2 catalyst shows a satisfactory de-NO_x performance and stability under 300–400 ºC[3]. However, there still exists some problems, such as the formation of N_2O at high temperatures[4], and toxicity of vanadia. Therefore many efforts have been made to develop superior non-vanadium catalysts such as Fe, Mn and Cu oxides supported on TiO_2[5–8], as well as Fe or Cu exchanged zeolites[9,10]. In these studies, WO_3 mixed with TiO_2-anatase has been most widely used as the support material during the SCR of NO by NH_3 because of its remarkable surface acidity and excellent sulfur tolerance structural strength of SCR monolith catalyst[11].

Recently, more attentions have been paid to cerium-based catalysts on account of the unique oxygen storage capacity and excellent redox properties[12]. Qi et al.[13] developed MnO_x-CeO_2 catalysts by different synthetic methods and obtained catalysts with favorable activities for NO_x reduction at low temperatures. Xu et al.[14] studied the deactivation effect of SO_2 and H_2O on Ce/TiO_2 catalyst and found that H_2O and SO_2 only had slight influence on the catalytic activity over Ce/TiO_2 catalyst. Peng et al.[15] prepared a series of CeO_2-WO_3/TiO_2 catalysts with different loadings of SiO_2 and demonstrated that SiO_2 had a positive influence on increasing the BET surface area and the amount of Brønsted acid sites of the catalysts. Nevertheless, these catalysts were mainly tested under relatively low gas hourly space velocity (GHSV) using sieved powders. As we know, the monolith catalyst is more representative for industrial application for it suffers low pressure drop, short diffusion distances and large geometric surface area[16].

As stated above, it is necessary to investigate the monolith CeO_2/TiO_2-SiO_2-WO_3 catalyst for SCR of NO with NH_3. In this study, a series of cerium modified TiO_2-SiO_2-WO_3 was prepared and applied as an NH_3-SCR monolith catalyst for the first time. And the characteristics of CeO_2/TiO_2-SiO_2-WO_3 catalysts and their SCR performances under a high GHSV were investigated.

1 Experimental

1.1 Catalyst preparation

TiO_2-SiO_2-WO_3 was prepared by a co-precipitation method with a mass ratio of 80:10:10 ($TiO_2/SiO_2/WO_3$= 8/1/1). To prepare TiO_2-SiO_2-WO_3, a mixture of

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$TiOSO_4·2H_2O$, SiO_2 sol and $(NH_4)_6H_2W_{12}O_{40}·xH_2O$ was dissolved in distilled water. An aqueous solution of ammonia was used as the precipitator and was added dropwise to the metal salt solution (pH=9.0). The resulting precipitate was filtered, washed, and dried at 110 ºC overnight, and then was calcined at 550 °C in air for 2 h.

A series of CeO_2/TiO_2-SiO_2-WO_3 monolith catalysts was prepared by impregnating the TiO_2-SiO_2-WO_3 powder with $Ce(NO_3)_3·6H_2O$ aqueous solution. The amounts of cerium oxides were 0 wt.%, 5 wt.%, 10 wt.% and 15 wt.%, respectively. The obtained samples were firstly dried at 110 °C overnight and then calcined at 550 °C for 2 h in air. Afterwards, the above powders were mixed with distilled water containing different amounts of certain to form well-proportioned slurries, respectively. The slurries were coated onto honeycomb cordierites with the size of 2.7 cm (length)×0.55 cm (radius) with a cell density of 400 cpsi supplied by Corning Ltd. (2.5 cm^3), the loading amount was about 150 g/L. And these monolithic catalysts were calcined at 550 °C for 2 h in air and were labeled as Cata-1, Cata-2, Cata-3 and Cata-4, respectively.

1.2 Catalytic activity measurement

The catalytic activity measurement was carried out in a fixed-bed quartz flow reactor. Reactant gases were regulated by mass-flow controllers before entering the reactor. The concentrations of the simulated gases were as follows: 1000 ppm NO, 1000 ppm NH_3, 5% O_2, 5% H_2O (when used), 100 ppm SO_2 (when used) balanced with N_2, the gas hourly space velocity (GHSV) was 30,000 h^{-1} and the total flow rate was about 1250 mL/min. The NO and NO_2 concentrations in inlet and outlet gas were continually analyzed by chemiluminescent NO/NO_x analyzer (Model 42i, Thermo Inc). And N_2O concentrations were detected by FT-IR (Antaris IGS, Nicolet). To avoid the influence caused by ammonia, the outlet stream was passed through an ammonia trap containing phosphoric acid solution before entering the analyzer. The data were recorded after the temperature was maintained for 30 min at every testing point.

The NO_x conversions and N_2 selectivity (S_{N_2}) were calculated as follows:

$$NO_x\ \text{conversion} = \left(1-\frac{[NO_x]_{out}}{[NO_x]_{in}}\right)\times 100\% \qquad (1)$$

$$N_2\ \text{selectivity} = \frac{[NO]_{in}+[NH_3]_{in}-[NO_2]_{out}-2[N_2O]_{out}}{[NO]_{in}+[NH_3]_{in}}\times 100\% \qquad (2)$$

1.3 Catalyst characterization

N_2 adsorption-desorption (BET) at –196 °C was performed on a QUADRASORB SI automatic surface analyzer (Quantachrome Inc). The samples were pretreated at 300 °C for 3 h prior to the measurement.

X-ray diffraction (XRD) data were collected on a D/max-rA diffractometer （Japan science）using Cu Kα (λ=0.15406 nm) radiation. The tube voltage and current were 40 kV and 100 mA, respectively. The X-ray powder diffractogram was recorded at an interval of 0.03 (º)/s in the range of 10º–80º.

The X-ray photoelectron spectroscopy (XPS) experiments were carried out on a spectrometer (XSAM-800, KRATOS Co.) with Al Kα radiation under 13 kV high pressure and 20 mA electric current. The C 1s peak (284.8 eV) was used for the calibration of binding energy values.

The surface morphology and elemental composition of the samples were observed by a scanning electron microscope (SEM, Hitachi S4800) combined with an energy dispersive X-ray spectroscopy (EDS) attachment. The accelerating voltage was 5.0 kV.

2 Results and discussion

2.1 Catalytic activity

The catalytic activity of different monolith catalysts for the SCR of NO by NH_3 is shown in Fig. 1(a). The NO_x conversion curves show that the NH_3-SCR reaction has an activity temperature window, indicating the conversion of catalysts increases firstly and subsequently decreases with the temperature increasing. The NO_x conversion is affected noticeably by the loading of CeO_2 in the reaction temperature range. Combined Fig. 1(a) with Table 1, the light-off temperature T_{50} (the temperature at which NO_x conversion reaches 50%) of Cata-1 is 299 °C, and the maximum NO_x conversion is 89% at 399 °C, then the conversion decreases to 50% at 504 °C. Although the NO_x conversions enhance obviously by mixing SiO_2 to WO_3/TiO_2 compared with the earlier study of WO_3/TiO_2 by Kobayashi et al.[17] , there is no complete conversion temperature T_{90} (the temperature at which NO_x conversion reaches 90%) of NO_x. It should be noted that the addition of cerium has a novel promoting effect on the catalytic activity for NO_x reduction within the whole temperature range (238–550 ºC). The T_{50} and T_{90} of Cata-2 are 258 and 299 °C, respectively. So ΔT (ΔT= T_{90}–T_{50}) of this catalyst is 41 °C, and the maximum NO conversion reaches 99% at 353 °C, which is much higher than that of Cata-1. Moreover, the activity temperature window of ΔT_{90} (the temperature range at which the NO conversion reaches 90%) is 217 °C. This result indicates that a synergistic effect for the NH_3-SCR reaction might exist between Ce species and Ti species[18]. With the cerium oxides loading increasing (10 wt.%), the T_{50} and T_{90} of Cata-3 are 240 and 277 °C, respectively, so ΔT is only 37 °C, and the maximum NO_x conversion is 99% at 307 °C. Moreover, ΔT_{90} is 235 °C, showing a wider tempera-