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Influence of calcination temperature on selective catalytic reduction of NO_x with NH_3 over CeO_2-ZrO_2-WO_3 catalyst

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Abstract: A series of CeO_2-ZrO_2-WO_3 catalysts for the selective catalytic reduction (SCR) of NO with NH_3 were prepared by hydrothermal method. The influence of calcination temperature on the catalytic activity, microstructure, surface acidity and redox behavior of CeO_2-ZrO_2-WO_3 catalyst was investigated using various characterization methods. It was found that the CeO_2-ZrO_2-WO_3 catalyst calcined at 600 ºC showed the best catalytic performance and excellent N_2 selectivity, and yielded more than 90% NO conversion in a wide temperature range of 250–500 ºC with a space velocity (GHSV) of 60000 h^{-1}. As the calcination temperature was increased from 400 to 600 ºC, the NO conversion obviously increased, but decreased at higher calcination temperature. The results implied that the higher surface area, the strongest synergistic interaction, the superior redox property and the highly dispersed or amorphous WO_3 species contributed to the excellent SCR activity of the CeO_2-ZrO_2-WO_3 catalyst calcined at 600 ºC.

Keywords: CeO_2-ZrO_2-WO_3; selective catalytic reduction; calcination temperature; amorphous; synergistic interaction; rare earths

Nitrogen oxide (NO_x) is harmful to the environment and humans[1,2]. Selective catalytic reduction of NO_x by NH_3 is regarded as the most effective method for removal of NO_x[3]. Nowadays, many efforts have been focused on the development of new NH_3-SCR catalysts because of some inevitable disadvantages of commercial V_2O_5/TiO_2 (promoted by WO_3 or MoO_3) catalyst, such as the narrow activity temperature window of 300–400 ºC, the low N_2 selectivity at high temperature and the toxicity of vanadium pentoxide[4–7]. Therefore, an efficient and environmental-friendly catalyst is urgently needed for abatement of NO_x emitted from diesel engine.

Recently, ceria-based catalysts have been investigated sufficiently in NH_3-SCR reaction for its oxygen storage and redox properties by translation of $Ce^{4+}\leftrightarrow Ce^{3+}$ [8,9]. However, the SCR performance of CeO_2 is very poor. Doping other transitional metals can dramatically improve the SCR activity of CeO_2[10,11], such as CeO_2/TiO_2[12], CeO_2/Al_2O_3[13], MoO_3/CeO_2 mixed oxides, etc[14]. Furthermore, the addition of Zr into CeO_2 can lead to the generation of oxygen vacancies, and then significantly improves the catalytic activity. Besides, the introduction of WO_3 into the CeO_2-based catalysts results in more abundant Ce^{3+} and strengthens surface acidity, which improves the SCR activity of catalysts[15]. Li et al.[16] have reported that a WO_3/CeO_2-ZrO_2 catalyst prepared by incipient impregnation exhibited high activity at 300–500 ºC. The CeO_2-ZrO_2-WO_3 catalyst with surpassingly hydrothermal stability has attracted much attention as a potential SCR catalyst for removal of NO_x emitted from diesel engine.

In this work, the CeO_2-ZrO_2-WO_3 catalysts prepared by hydrothermal method yielded more than 90% NO conversion at 250–500 ºC. However, the surface area, the crystallite size distribution and the catalytic properties were strongly dependent on the calcination temperature. Besides, the exhaust temperature of diesel engine equipped with a diesel particulate filter (DPF) is often in a dynamic temperature range of 200–740 ºC. Thus the SCR reaction temperature may suddenly rise up in some working conditions, resulting in the structural change and activity decline of catalyst. Therefore, the influence of calcination temperature on the SCR properties is well worthy to be discussed. However, few works have been done on the use of CeO_2-ZrO_2-WO_3 catalyst to investigate the reactive characteristics of different active species in NH_3-SCR reaction with various calcination temperatures. Hence, the reactive characteristics of CeO_2-ZrO_2-WO_3 catalysts calcined at different temperatures were investigated by H_2-TPR, XRD, N_2 adsorption-desorption, HR-TEM, NH_3-TPD, RS and XPS.

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1 Experimental

1.1 Catalysts preparation

The samples were prepared by the improved hydrothermal method. All chemicals used were of analytical reagent grade. $Zr(NO_3)_4{\cdot}xH_2O$ (4.2924 g), $Ce(NO_3)_3{\cdot}6H_2O$ (4.3412 g) and $(NH_4)_6H_2W_{12}O_{40}{\cdot}6H_2O$ (0.6491 g) were dissolved in acrylic acid (2.16 g) and glucose (9.9 g) solution, which was beneficial to the generation of mesostructure, resulting in improvement of specific surface area, as has been proved by Li et al.[17]. Then, an ammonia solution (26 wt.%) was dropwise poured into the above mixture with vigorous stir until the pH reached 10. Subsequently, the mixture was stirred for 5 h at room temperature. After that, it was moved into a Teflon-lined, stainless autoclave at 160 ºC for 72 h. The final sample obtained was filtered, washed, and dried at 80 ºC for 12 h before it was calcined at different temperatures ranging from 400 to 800 ºC for 5 h in air. The catalysts thus obtained are correspondingly denoted as CZW-4, CZW-5, CZW-6, CZW-7 and CZW-8, respectively.

1.2 Catalysts characterization

The powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/Max 2500 system between 10º and 70º at a step of 2 (º)/min for determining the crystal structure by using Cu Kα (40 kV, 100 mA) radiation. Raman spectra were carried out on a Renishaw-2000 Raman spectrometer at a resolution of 2 cm^{-1} by using the 514.5-nm line of an Ar ion laser as the excitation source. The high- resolution transmission electron microscopy (HR-TEM) with high magnification was conducted on a JEOL JEM- 2100 analytical transmission electron microscope using an accelerating voltage of 200 kV to obtain the microscopic structures.

The specific surface area was evaluated with Brunauer-Emmett-Teller (BET) model by N_2 adsorption at –196 ºC on a Tristar II 3020 automated gas sorption system. The samples were pretreated at 300 ºC for 4 h prior to the measurement. X-ray photoelectron spectroscopy (XPS) was performed in an ULVAC PHI 5000 Versa Probe-II equipment operating at 10^{-9} Pa with an Al Ka radiation (1486.6 eV) to analyze the surface atomic concentration and characterize the chemical states of the catalysts. The observed spectra were corrected with the C 1s binding energy value of 284.8 eV.

The H_2 temperature-programmed reduction (H_2-TPR) and the NH_3 temperature-programmed desorption (NH_3-TPD) experiments were performed on a GC-9750 with 0.05 g of the catalyst. Prior to the H_2-TPR experiments, the samples were pretreated in pure N_2 at 400 ºC for 45 min and cooled to room temperature. The H_2-TPR runs were performed in a flow of 5 vol.% H_2/Ar (30 mL/min) from room temperature to 900 ºC with a heating rate of 10 ºC/min. For the NH_3-TPD experiments, after pretreatment in pure He at 400 ºC for 45 min, the catalyst was cooled to 100 ºC in pure He followed by saturation for 45 min with a stream of NH_3(4%)/He. After saturation, the catalysts were flushed in a pure He flow for 20 min at 100 ºC. Finally, the NH_3-TPD was carried out in pure He at a heating rate of 10 ºC/min from 100 to 800 ºC. The NH_3 desorption (or H_2 uptake) was detected by a thermal conductivity detector (TCD).

1.3 Activity test

The NH_3-SCR activity measurements were performed in a fixed-bed quartz reactor (9 mm i.d.) with 0.4 mL catalysts of 60–80 mesh. The gas flow was monitored by mass flow meters. The basic composition of feed gas included 600 ppm NH_3, 600 ppm NO, 5 vol.% O_2 and N_2 as the balance gas at a flow rate of 400 mL/min for accurately reflecting the influence of calcination temperature on the NO conversion over the CZW catalysts. The concentration of NO was continuously detected by a flue gas analyzer (ECOM·J2KN). The reaction system was maintained for 30 min at each reaction temperature before analysis. The N_2O product was analyzed using gas chromatograph (Fuli, 9790) equipment with an electron capture detector.

2 Results and discussion

2.1 NH_3-SCR performance of CZW catalysts

Fig. 1(a) presents the NH_3-SCR catalytic activity results of CeO_2-ZrO_2-WO_3 catalysts calcined at different temperatures. The results indicated that the calcination temperature significantly influenced the SCR activity. With the increase of calcination temperature, the NO conversion increased until the calcination temperature reached 600 ºC. After this level, a further increase of calcination temperature led to the decrease of NO conversion. From Fig. 1(a), it could be seen that the CZW-6 presented the highest SCR activity, and over 80% NO conversion was obtained at 250–525 ºC. CZW-4 and CZW-5 showed an excellent performance at the relativity narrow working temperature window, and CZW-7 showed relatively low NO conversion below 300 ºC. The inferior NO conversion was observed over CZW-8, and only more than 80% NO conversion was obtained in a narrow temperature range of 375–525 ºC. These phenomena indicated that the calcination temperature had a significant influence on NH_3-SCR activity of the samples.

The N_2 selectivity was one of the most important factors for the practical application of a SCR catalyst during NH_3-SCR process. The results of N_2 selectivity in the NH_3-SCR reaction were measured and it is presented in Fig. 1(b). N_2O yield was very low for CZW catalysts, even negligible if compared with the high NO_x conversion.