SO_2 tolerance of the CeO_2-TiO_2 catalyst for selective catalytic reduction of NO_x by NH_3

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Abstract: Ceria-based (CeO_2-TiO_2) catalysts were prepared by dry ball milling method with $Ce_2(C_2O_4)_3$ as precursor and TiO_2 was chosen as a carrier. The prepared CeO_2-TiO_2 catalyst was treated in reaction atmosphere with addition of 1500 ppm SO_2 in 40 and 60 h, respectively. The performances of selective catalytic reduction (SCR) of NO with NH_3 as the reductant over the fresh and treated samples were investigated.

Keywords: CeO_2-TiO_2, selective catalytic reduction, SO_2, ball milling.

1. Introduction

The selective catalytic reduction process (SCR) of NO_x with ammonia as reductant was commonly recognized as an available method to eliminate NO_x in flue gasses. Ceria based catalyst has been awarded widely attentions and investigated for SCR in the nearly decades [1]. In this process, the catalyst preparation is a relevant issue to meet the future need, which depended on the activity and economy. As a simple method, dry ball milling was selected to fabricate CeO_2-TiO_2 catalysts nearly [2]. It was found that the catalysts prepared by ligand-assisted ball milling exhibited high NH_3-SCR activities due to the interaction between cerium ions and ligand molecules resulting in good dispersion, a high Ce^{3+} ratio and high reducibility of cerium species. Usually, the flue gas contains sulfur. As CeO_2-TiO_2 materials used as SCR catalyst for NO_x elimination, the performance and SO_2 resistance cannot neglected.

2. Experimental

The CeO_2-TiO_2 catalysts were synthesized from a cerium precursor ($Ce_2(C_2O_4)_3$) and titania (TiO_2) by a dry ball milling protocol in room temperature, which was a two-step process, including the milling step and the calcination step of the milled mixture. The details were similar to that reported [2]. The sample after calcination was labelled as CeO_2-TiO_2-fresh, and the samples after used in the flue gas 40 h and 60 h were labelled as CeO_2-TiO_2-40h and CeO_2-TiO_2-60h, respectively.

X-ray photoelectron spectra (XPS) were performed on an X-ray photoelectron spectrometer (Thermo Fisher, ESCALAB 250 Xi), using monochromatic Al Kα radiation (1486.6 eV) operating at an accelerating power of 15 kW.

The NH_3-SCR activities of the samples for NO selective catalytic reduction were evaluated in a quartz micro-reactor (id = 8 mm) at atmospheric pressure. The flow rate of reactant mixture of 1000 ppm NO, 1000 ppm NH_3, 6% O_2, 175 ppm SO_2, 6 % H_2O, He balance, and the space velocity was 30,000 h^{-1}.

3. Results and discussion

The NH_3-SCR activities over the three samples are investigated and the results are summarized in Fig. 1. It shows that the NO conversions over the CeO_2-TiO_2-fresh, CeO_2-TiO_2-40h and CeO_2-TiO_2-60h samples increased as the reaction temperature rising and reached their maximum at ca. 300, 350 and 350 ^{o}C, respectively, implying that the deactivation of CeO_2-TiO_2-fresh in the flue gas in 40 h. CeO2 may reacted with SO_2 in the process to give cerium sulfate [3]. One can also find that the similar activity was presented in Fig. 1, which showed that after the process of deactivation in the flue gas, the activity could be hold in a relative stable level.

However, as the temperature increased, higher than 350 °C, NO conversions over the three samples were so close (more than 95%). It exhibited that the transition from CeO_2 to cerium sulfate inhibited the reduction of NO in the relative low temperature (lower than 350 °C).

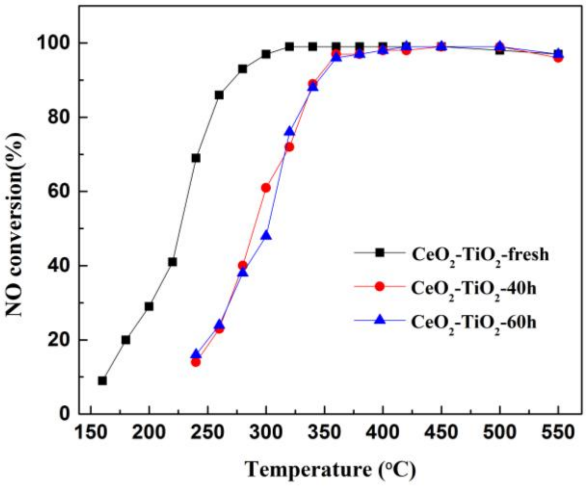

Figure 1. NO conversion over the samples CeO_2-TiO_2-fresh, CeO_2-TiO_2-40h, CeO_2-TiO_2-60h
Reaction condition: 1000 ppm NO, 1000 ppm NH_3, 6% O_2, 175 ppm SO_2, 6 % H_2O, He balance, GHSV: 30,000 h^{-1}

In order to investigate the composition and the surface atomic concentrations of the samples, the XRF and XPS characterizations were carried out and the result was summarized in Table 1. For the fresh sample, only 0.41% SO_3 (calculated as oxide) was detected, and after reaction for 40 h, the SO_3 content was increased to 6.32%, implying that sulfate were formed in the reaction process. When prolong the reaction period to 60 h, the SO_3 content of CeO_2-TiO_2-60h was similar as that of CeO_2-TiO_2-40h.

The surface Ce concentrations over the fresh sample decreased from 2.6% to 1.4%, and the S concentrations increased from 1.2% to 4.2% after the reaction for 40 h, suggesting the sulfate existed in the surface. When the reaction time prolonged, the surface atomic concentration over the catalyst changed little.

Table 1. Compositions and the surface atomic concentrations over of the samples measured by XRF and XPS, respectively.

Samples	Component content (wt%)			Surface atomic concentration (%)		
	TiO_2	CeO_2	SO_3	Ce	O	S
CeO_2-TiO_2-fresh	67.5	31.8	0.41	2.6	63.6	1.2
CeO_2-TiO_2-40h	61.5	31.8	6.32	1.4	65.3	4.2
CeO_2-TiO_2-60h	62.1	31.7	5.83	1.4	64.9	3.9

4. Conclusions

From the results of performance evaluation, one can realize that the CeO_2 reacted with SO_2 to give cerium sulfate in the flue gas, which inhibited the reduction of NO by NH_3 in the low temperature (lower than 350 °C). As the same time, after a period reaction, the activity of CeO_2-TiO_2 catalyst could maintain in the flue gas containing SO_2 and H_2O.

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