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Influence of alkali earth metals on Ce/TiO$_2$ catalyst for selective catalytic reduction of NO with NH$_3$

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Abstract. The salts of alkali earth metals (Ca and Mg) in fly ash have a deactivation effect on SCR catalyst. In this study, the poisoning effect of Ca and Mg on Mn/TiO$_2$ catalyst was investigated and explained based on experimental and characterization results of BET, XRD, H$_2$-TPR, NH$_3$-TPD and XPS. It was found that the deactivation effect of Ca is more obvious than that of Mg. The results showed that the drop of redox ability and Brønsted acidity, and the decrease of active oxygen species led to the decrease of Ca-Ce/TiO$_2$ and Mg-Ce/TiO$_2$.

1 Introduction

Selective catalytic reduction process, as the most effective method for controlling NOx emission from the stationary sources, has been put into widely commercial application [1-3]. Because the classic vanadium-based catalyst is expensive and not environmental friendly, much attention has been put into developing green environmental SCR catalyst in recent years.

During the past several years, the oxides of some transitional metals (Mn, Ce, Cu and Fe, etc.) have been used as the active components of SCR catalyst and show high activity [1, 3-10]. Among them, cerium oxide has drawn much attention due to its high oxygen storage capacity and excellent redox property [11]. The study of Shan et al. [12] found that the CeO$_2$/TiO$_2$ catalyst prepared by an optimized homogeneous precipitation method was of excellent NH$_3$-SCR activity and high N$_2$ selectivity within a broad operation temperature window. Therefore, cerium-based catalyst may be a potential choice for NH$_3$-SCR reaction in the future; but it is still necessary to study the influence of alkali earth metals in the fly ash of flue gas on Ce/TiO$_2$ catalyst.

The poisoning effect of alkali earth metal on vanadia-based catalyst has been studied thoroughly and many reports could be found in the literatures [13-15]. Recently, the influence of Ca on low temperature SCR catalyst has been deeply studied [15-17]. It is well known that Mg is another important alkali earth metal in the fly ash of coal-fired power plants. However, the effect of Mg on the performance of low temperature SCR catalyst is still not available in literatures. Consequently, the effect of Ca and Mg on Ce/TiO$_2$ catalyst was investigated in this study based on experimental and characterization results.

2 Experimental

2.1 Catalyst preparation

Ce/TiO$_2$ catalyst was prepared by using sol-gel method, as described in our previous paper [18]. Ca and Mg were added to the fresh Ce/TiO$_2$ catalyst by impregnation from Ca(NO$_3$)$_2$ and Mg(NO$_3$)$_2$ solutions with a certain concentration. The detailed procedure was also given in reference [18]. The molar ratio between Ce and Ti in the fresh catalyst was set as 0.35:1, and the molar ratio between Ca (or Mg) and Ce in the poisoned catalyst was set as 0.5:1.

As a matter of convenience, the fresh catalyst and the poisoned catalysts are denoted as Ce/TiO$_2$, Ca-Ce/TiO$_2$ and Mg-Ce/TiO$_2$ respectively.

2.2 Characterization

The BET results were measured by N$_2$ adsorption at 77 K using a Quantachrome Autosorb-iQ-AG instrument. The crystal structure of the catalyst samples was determined by using an X-ray diffractometer (XRD) with Cu Kα radiation (Bruker D8 Advance). The redox property of the catalyst samples was measured by using temperature programmed reduction (H$_2$-TPR) method. And temperature programmed desorption (NH$_3$-TPD) was performed to study the surface acidity of the catalyst samples. All the experiments of TPR and TPD were performed on a Quantachrome Autosorb-iQ-C chemisorption analyzer. And the signals of H$_2$ and NH$_3$ were recorded on a thermal conductivity detector (TCD). To obtain the chemical states for all elements on the catalyst surface, X-ray photoelectron spectroscopy (XPS) was carried out a Thermal ESCALAB 250 spectrometer with Al Kα X-ray. The shift of the binding energy caused by relative surface charging was calibrated based on the C1s level at 284.8 eV as an internal standard.

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2.3 Activity test

The catalytic activities of the catalyst samples for selective catalytic reduction of NO with NH_3 were tested on a fixed bed reactor (i.d. 8 mm) with 0.55 cm^3 catalyst of 100-120 mesh. The simulated flue gas contains the following components: 600 ppm NO, 600 ppm NH_3, 5% O_2, and balance with Ar. In each experimental run, the flowrate of simulated flue gas was kept at 1L/min with a gas hourly space velocity of 108, $000h^{-1}$. To calculate the SCR activities of the catalyst samples, a NO–NO_2–NOx analyzer (Thermo, Model 42i-HL) was used to monitor the concentration of NO and NO_2 in the inlet and outlet simulated flue gas. The concentration of N_2O was continuously analyzed by an online Nicolet 6700 FTIR spectrometer equipped with a gas cell with 0.2 L volume.

3 Results and discussion

3.1 SCR activity

Fig.1 illustrates the NO conversions over the fresh and poisoned catalyst samples within the temperature range of 150-450 °C. As expected, Ce/TiO_2 catalyst shows a high SCR activity in a broad temperature window. After the addition of Ca or Mg, an obvious activity drop of Ce/TiO_2 catalyst can be observed, and the poisoning effect of Ca seems more serious than that of Mg, especially in the higher reaction temperature range. For instance, when the reaction temperature is 400 °C, the addition of Mg causes the SCR activity of Ce/TiO_2 decrease from 100% to 96.47%, while the SCR activity of Ca-Ce/TiO_2 at 400 °C is only 62.05%. In the following sections, we will explain the different poisoning effect of Ca and Mg on Ce/TiO_2 catalyst based on the characterization results.

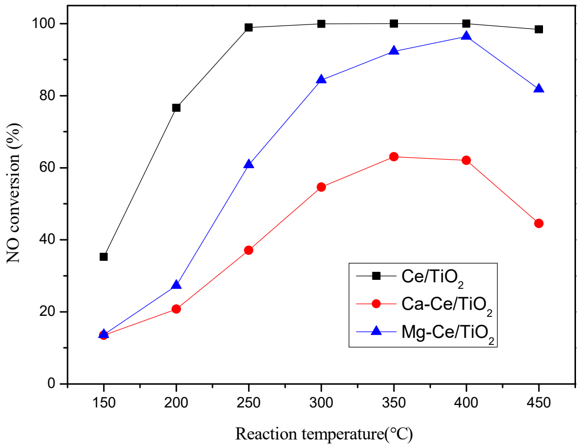

Fig.1. NO conversions over the three catalyst samples Reaction conditions: [NO]=[NH_3]=600 ppm, [O_2] = 5%, balance Ar, GHSV=108,000 h^{-1}

3.2 BET and XRD analysis

The results of BET measurements are summarized in Table 1. It can be concluded that the BET surface area and pore volume are decreased after the addition of Ca or Mg, and Ca-Ce/TiO_2 exhibits the smallest surface area and pore volume among the three catalyst samples. The decrease of surface area and pore volume for Ca-Ce/TiO_2 and Mg-Ce/TiO_2 may be caused by the coating of Ca or Mg species to the sample, which could block the microspores on the surface of Ce/TiO_2 catalyst and cause the decrease of surface area and pore volume. Furthermore, because the radii of Ca^{2+} (0.1nm) and Mg^{2+} (0.072nm) are larger than that of Ti^{4+} (0.061nm), the doping of Ca or Mg would lead to an increase of pore diameter, as presented in Table1.

Table 1. BET measurements for the three catalyst samples

Samples	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
Ce/TiO_2	181.16	0.2550	2.167
Ca-Ce/TiO_2	86.55	0.1475	2.451
Mg-Ce/TiO_2	105.72	0.1867	2.814

The crystal structures of the three catalyst samples were investigated by XRD analysis. As can be seen from Fig.2, there are no diffraction peaks corresponding to CeO_2 could be observed on the XRD patterns of the three catalyst samples, indicating the highly dispersion of Ce species on the surface of TiO_2. Besides that, it should be noticed that the diffraction peaks of rutile TiO_2 and anatase TiO_2 become weaker after the doping of Ca or Mg. Some other researchers also found a similar phenomenon when they studied the effect of Ca doping on the crystal structure of SCR catalyst [17]. As mentioned above, the radii of Ca^{2+} and Mg^{2+} are larger than that of Ti^{4+}. As a result, when Ca^{2+} or Mg^{2+} is intercalated into the TiO_2 lattice, an expansion of TiO_2 lattice would happen, leading to the decrease of TiO_2 crystallinity.

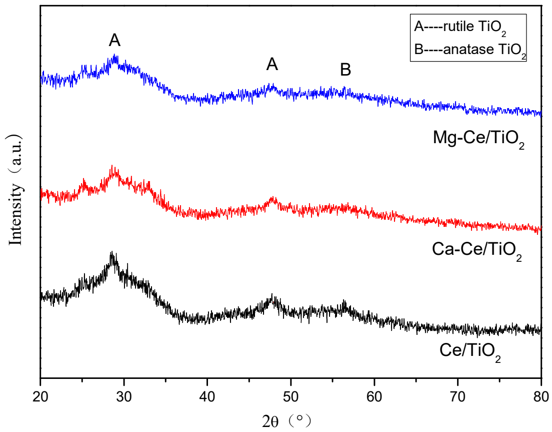

Fig.2. XRD profiles of the three catalyst samples

3.3 H_2-TPR analysis

H_2-TPR analysis was carried out to investigate the doping of alkali earth metals on the redox behavior of Ce/TiO_2 catalyst, and the results are presented in Fig.3. As illustrated in Fig.3, there are two reduction peaks in the H_2-TPR profile of each catalyst. The first peak and the second peak in the profile of each catalyst sample are of the similar nature: the first one can be attributed to the reduction of amorphous CeO_2 on the surface of TiO_2, and the second one can be assigned to the reduction of bulk

CeO_2 [16]. Furthermore, it could be found that the reduction peaks shift to higher temperature, thus the addition of Ca or Mg can reduce the degree of reduction of the cerium species. In addition, the reduction peak of surface CeO_2 in the profile of Mg-Ce/TiO_2 are much broader and more intensive than that in the profiles of Ce/TiO_2 and Ca-Ce/TiO_2. This could contribute to the relatively higher SCR activity in the temperature range of 300-450°C over Mg-Ce/TiO_2.

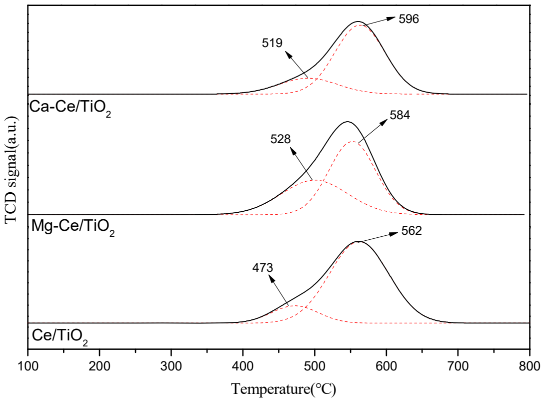

Fig.3. H_2-TPR profiles of the three catalyst samples

3.4 NH$_3$-TPD analysis

The surface acidities of the three catalyst samples are studied by using NH_3-TPD analysis and the results are shown in Fig.4. It is noticeable that there are two main desorption peaks on the profile of each catalyst. The first one lasting from 100-500°C could be related to Brønsted acid sites [19], and the second one in the temperature range of 600-750°C could be ascribed to Lewis acid sites [20]. It is clear that the addition of Ca or Mg could lead to a great decrease of Brønsted acidity of Ce/TiO_2 catalyst, while the inhibition effect of Ca and Mg on Lewis acidity is relatively weaker. The results are in accordance with Chen et al. [14], and they also found that the weak acid sites on V/TiO_2 catalyst were neutralized much more heavily than the strong acid sites after the addition of Ca or Mg. It is important to note that the inhibition effect of Mg on Brønsted acidity is much weaker than that of Ca, which is in good agreement with their different poisoning effect on Ce/TiO_2 catalyst.

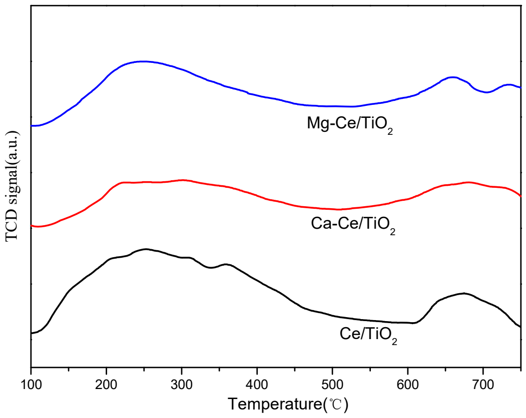

Fig.4. NH_3-TPD profiles of the three catalyst samples

3.5 XPS analysis

The chemical states of the elements in the near-surface region of the catalyst sample were investigated by XPS analysis, and the XPS spectra of O1s are illustrated in Fig.5. The O1s spectra could be deconvoluted into two peaks. The peak with a binding energy at 530.0eV could be assigned to lattice oxygen bonded to Mn (denoted as O_α), and the peaks at 530-536eV could be attributed to the surface adsorbed oxygen and surface hydroxyl groups (denoted as O_β) [21,22]. The calculated ratios of $O_\beta/(O_\alpha+O_\beta)$ for Ce/TiO_2, Ca-Ce/TiO_2 and Mg-Ce/TiO_2 are 51.0%, 40.0% and 45.0% respectively. It is well recognized that O_β is the active oxygen species due to its high mobility. High $O_\beta/(O_\alpha+O_\beta)$ ratio can promote the oxidation of NO to NO_2 [23], as a result, facilitating the so-called "fast SCR" reaction[24]. Therefore, the decreased $O_\beta/(O_\alpha+O_\beta)$ ratio for Ca-Ce/TiO_2 and Mg-Ce/TiO_2 should be another reason for their low SCR activities.

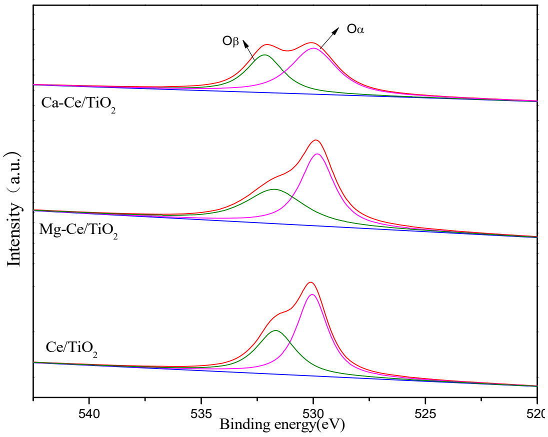

Fig.5. XPS spectra of O1s for different catalyst samples

4 Conclusions

Both of Ca and Mg have a poisoning effect on Ce/TiO_2 catalyst for selective catalytic reduction of NO with NH_3. And the deactivation effect of Ca is more serious. From the results of characterization, we may conclude that the drop of redox ability and Brønsted acidity, and the decrease of active oxygen species should be the main factors resulting in the decline of NH_3-SCR activity of Ce/TiO_2 catalyst after the addition of Ca or Mg.

Acknowledgements

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