

Effect of K and Ca on catalytic activity of Mn-CeO_x/Ti-PILC

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Abstract Mn-CeO_x/Ti-pillared clay (PILC) is an attractive catalyst for selective catalytic reduction of NO_x at low temperature because of its low cost. The poisoning of K and Ca on the catalyst of Mn-CeO_x/Ti-PILC is an important problem because K and Ca are always in presence in flue gas. To investigate the effect of K and Ca on the physicochemical characters of the catalysts, the techniques of NH₃-temperature programmed desorption (TPD), H₂-temperature programmed reduction (TPR), and X-ray photoelectron spectroscopy (XPS) were used to analyze the fresh and deactivated catalysts of Mn-CeO_x/Ti-PILC. (Ca)Mn-CeO_x/Ti-PILC and (K)Mn-CeO_x/Ti-PILC are denoted for the dopes of the catalyst of Mn-CeO_x/Ti-PILC with Ca and K, respectively. The activities of Mn-CeO_x/Ti-PILC, (Ca)Mn-CeO_x/Ti-PILC and (K)Mn-CeO_x/Ti-PILC for NH₃-selective catalytic reduction (SCR) reaction at low temperature were investigated. The results showed that with the dopes of K and Ca on the catalysts, the SCR activities of the catalysts decreased greatly, and K exhibited more poisoning effect than Ca. With the dopes of K and Ca, the acidity, the redox property and chemisorbed oxygen on the surfaces of the catalysts were decreased, which resulted in a decreasing in SCR activity.

Keywords Mn-CeO_x/Ti-pillared clay (PILC), low-temperature selective catalytic reduction (SCR), K and Ca poisoning effect

1 Introduction

It is well known that NH₃-selective catalytic reduction (SCR) is one of the most successful methods to eliminate NO_x in flue gases from stationary combustion system [1,2]. Mn-CeO_x based catalysts have been shown to be active for low-temperature SCR of NO with NH₃, so the topic about catalytic activity, selectivity and resistance to SO₂ and H₂O for the catalysts based on Mn-CeO_x have been studied

extensively [3–6].

Alkali metal such as K or alkaline-earth metal such as Ca is always in present in the flue gas from coal or biomass combustion. The concentration of K or Ca may also be enhanced in the flue gas when the desulfurization system is considered. The effect of alkali metal and alkaline-earth metal on the catalysts was focused in recent years. It showed that V₂O₅/WO₃-TiO₂, as a typical commercial SCR catalyst at middle temperature (300°C–400°C), can be deactivated by alkali and alkaline-earth metals in the flue gases [7–9]. Alkali and alkaline-earth were reported to interact with the acid sites of the V₂O₅ to reduce the adsorption of NH₃ in SCR process.

But until now, few studies have been devoted to the effect of the poisons on Mn-CeO_x based catalysts that are working under low temperature (80°C–260°C). Mn-CeO_x/Ti-pillared clay (PILC) is a promising catalyst with the introduction of Mn-CeO_x to Ti-pillared interlayer clays by impregnating method, which is demonstrated to have high active for low temperature SCR [10]. We are now very interested in what is the action of alkali and alkaline-earth metals on the catalyst of Mn-CeO_x/Ti-PILC, in order to find regeneration methods for the deactivation catalysts in the future studies. To study the effect of alkali and alkaline-earth metals on Mn-CeO_x/Ti-PILC, potassium and calcium with high concentrations were selected as the poisoning agents to discover the changes of physicochemical characters on the surfaces of the catalysts. Different methods, such as temperature-programmed desorption of NH₃ (NH₃-TPD), hydrogen temperature-programmed reduction (H₂-TPR), and X-ray photoelectron spectroscopy analysis (XPS) combined with the activity test of selective catalytic reduction of NO by NH₃ at low temperature were used to discover the changes.

2 Experiment

2.1 Catalyst preparation

The clay was bentonite (analytical grade, Guangfu company, China), with a cations exchange capacity of

86 mmol·(100 g)⁻¹. Ti-PILC was prepared as follows: the pillaring solution was prepared with dissolving tetranbutyl titanate in 5 mol·L⁻¹ HCl to obtain a molar ratio of HCl/Ti at 2. The mixture was stirred at room temperature for 30 min, kept for 3 h, and then dropped to an aqueous-acetonic (50 vol.%) clay suspension (1 wt.%) to obtain the value of 15 mmol Ti·g⁻¹ clay. The mixture was kept under vigorous stirring for 6 h at room temperature. After 12 h, the mixture was filtered, washed free of Cl dried at 110°C for 6 h and calcined at 400°C for 3 h yielding the TiO₂ pillared interlayer clay (Ti-PILC).

Mn-CeO_x/Ti-PILC (calculation as Mn₂O₃ loading of 6 wt.% and CeO₂ loading of 6 wt.%) was prepared by impregnating the Ti-PILC with an aqueous solution containing the required amount of manganese nitrate and cerium nitrate. The mixture was kept for 3 h, and then dried at 110°C for 6 h and calcined at 500°C for 3 h.

To study the effects of potassium and calcium on the catalyst, the poisoned catalysts were prepared by liquid-phase impregnation process [11]. K and Ca from the required amount of KNO₃ (molar ratio of K/Mn = 0.5), or Ca(NO₃)₂ (molar ratio of Ca/Mn = 0.5) with high enough concentrations were impregnated on Mn-CeO_x/Ti-PILC, respectively. Then the samples were dried in air at 110°C for 6 h and calcined at 500°C for 3 h. The samples poisoned by K and Ca were denoted as (K)Mn-CeO_x/Ti-PILC and (Ca)Mn-CeO_x/Ti-PILC, respectively.

2.2 SCR activity measurements

The SCR activity for NO removal by NH₃ was tested in a fixed-bed reactor. Four gas streams: 0.06 vol% NO, 0.06 vol% NH₃, 3 vol% O₂ and pure N₂ in balance were used. In all the runs, the total gas flow rate was maintained at 300 mL·min⁻¹ over 0.5 g catalyst (60–80 mesh) corresponding to a gas hourly space velocity (GHSV) of 80000 h⁻¹. The feed gases were mixed and preheated in a chamber before entering the reactor. During the measurements, the concentrations of NO at the inlet and outlet of the reactor were monitored by Flue Gas Analyzer (KM900/KM9106, Kane International Ltd., UK). The activities of the catalysts were expressed by the NO conversion (*X*) calculated as follows:

$$X = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\%, \quad (1)$$

where *C*_{in} and *C*_{out} are the NO concentration at the inlet and outlet of the fixed-bed reactor.

The activation of the catalyst was described by reaction rate constant *k* with first order which was calculated according to the rate expression below:

$$k = -\frac{F}{W} \ln(1-X), \quad (2)$$

where *k* is the reaction rate constant based on mass of

samples (cm³·g⁻¹·s⁻¹), *F* is the volume flow rate (mL·s⁻¹), *W* is the catalyst mass (g), *X* is the conversion of NO.

2.3 Catalyst characterization

NH₃-TPD and H₂-TPR were performed on tp-5080 automated chemisorption analyzer (Xianquan Company, China) using 0.1 g catalysts. The experiment of NH₃-TPD started with a pretreatment of the catalyst in pure N₂ at 500°C for 1 h. Subsequently, the catalyst was cooled down to room temperature in pure N₂ and then saturated for 30 min with a stream of pure NH₃ (flow rate at 30 mL·min⁻¹). After then, the catalysts were purged in a pure flow of N₂ for 30 min at 100°C. Finally, the NH₃-TPD was carried out in pure N₂ at a heating rate of 10°C·min⁻¹. The NH₃ desorption signal were measured quantitatively by a thermal conductivity detector.

In the H₂-TPR experiment, the sample was loaded into a quartz reactor and then pretreated in a flow of N₂ at 250°C for 0.5 h. After the sample was cooled down to room temperature in N₂, the reduction of the sample was carried out from room temperature to 700°C at a rate of 10°C·min⁻¹ in a flow of 5 vol% H₂/N₂ (30 mL·min⁻¹). The consumption of H₂ was monitored continuously with a thermal conductivity detector.

The atomic states on the surfaces of the samples were determined by XPS using Kratos Axis Ultra DLD spectrometer equipped with a monochromated Al Kα radiation (1486.6 eV) (Shimadzu Corporation, Japan). A multi-peak-resolution process for X-ray diffraction intensity curve using the software of XPS was carried out for further analysis.

3 Results and discussion

3.1 SCR activities of the catalysts

The activities of Mn-CeO_x/Ti-PILC, (K)Mn-CeO_x/Ti-PILC and (Ca)Mn-CeO_x/Ti-PILC measured at different temperatures from 80°C to 260°C at SCR conditions were shown in Fig. 1. The rate constant *k* for different catalysts is shown in Fig. 2. It can be seen that the catalyst of Mn-CeO_x/Ti-PILC showed high catalytic performance and the value of *k* increased sharply from 2.26 to 25.75 cm³·g⁻¹·s⁻¹ with increasing temperature from 80°C to 260°C. In comparison, the dope of Ca or K for the catalyst resulted in an obvious decrease of the values of *k*, which demonstrated that the presence of Ca or K on the surfaces reduced the activities of the catalysts sharply.

In comparison with the same molar ratio loading of K and Ca, (Ca)Mn-CeO_x/Ti-PILC showed a higher SCR activity than that of (K)Mn-CeO_x/Ti-PILC. The result indicated that K exhibited more poisoning effect than Ca. It was also found [12] that alkali as well as alkaline-earth

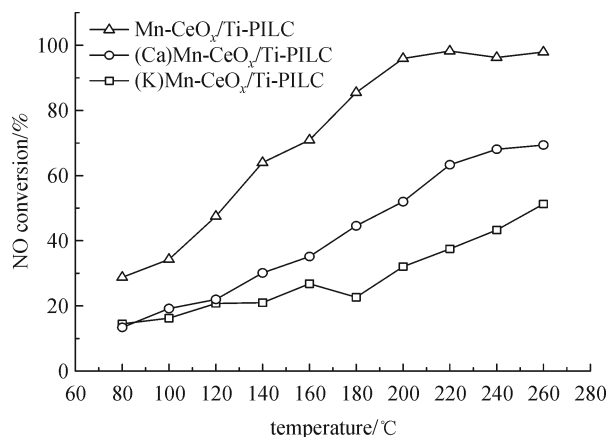


Fig. 1 NO conversion over the Mn-CeO_x/Ti-PILC, (K)Mn-CeO_x/Ti-PILC, and (Ca)Mn-CeO_x/Ti-PILC catalysts

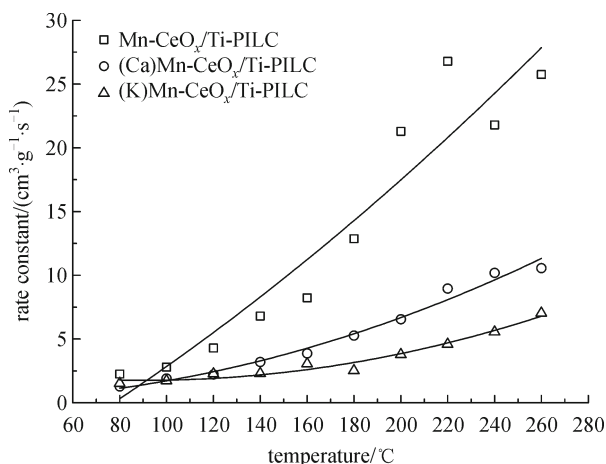


Fig. 2 SCR rate constant k at different temperatures over the Mn-CeO_x/Ti-PILC, (K)Mn-CeO_x/Ti-PILC and (Ca)Mn-CeO_x/Ti-PILC catalysts

metals were strong poisons to the V₂O₅ based SCR catalyst, and the deactivating effects decreased in the order of $K > Na > Ca > Mg$. The results are similar for Mn-CeO_x/Ti-PILC and V₂O₅. It is known that the alkalescence of K is higher than that of Ca. The high alkalescence on the surfaces of the catalyst might prevent the absorption of NH₃, which reduced the activities of the catalyst.

3.2 Surface acidities of the catalysts

It has been discovered that in the SCR reaction, ammonia is adsorbed on the acid sites to form NH₄⁺ or coordinated NH₃, then gaseous or adsorbed nitric oxides react with NH₄⁺ or coordinated NH₃ to form N₂ and H₂O. The adsorption of NH₃ on the surfaces of the catalyst is a control step for the SCR reaction [3,5]. So the catalysts that can adsorb large amount of NH₃ will exhibit good SCR activities. It is known that the adsorption of NH₃ is

determined by acidity on the surfaces of the catalysts, and NH₃-TPD is always used to detect the acidity of catalysts.

According to the results obtained by Lisi et al. [13], the adsorbing of ammonia at the temperature higher than 450°C was not involved in the SCR reaction. The NH₃-TPD was carried out to investigate the acidity for all three samples at the temperature of 100°C–500°C, as shown in Fig. 3. From Fig. 3, it showed that with at the temperatures increased from 100°C to 500°C, Mn-CeO_x/Ti-PILC, (K)Mn-CeO_x/Ti-PILC, and (Ca)Mn-CeO_x/Ti-PILC samples exhibited similar NH₃-TPD curves with one large peak. The adsorption amount of NH₃ can be linearly expressed as the integration of NH₃-TPD curves to the run time because NH₃-TPD for the experiments was running at the same conditions for the three catalysts. The integration values for the signals, that were linear with the acidities of the catalysts, were 2405, 2034 and 1714 for the Mn-CeO_x/Ti-PILC, (Ca)Mn-CeO_x/Ti-PILC and (K)Mn-CeO_x/Ti-PILC catalysts, respectively. The surface acidity of the catalysts was decreased in the order of as follows: Mn-CeO_x/Ti-PILC > (Ca)Mn-CeO_x/Ti-PILC > (K)Mn-CeO_x/Ti-PILC.

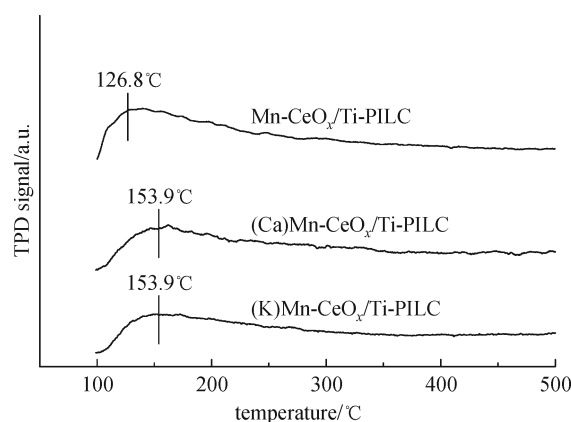


Fig. 3 NH₃-TPD profiles for Mn-CeO_x/Ti-PILC, (K)Mn-CeO_x/Ti-PILC, and (Ca)Mn-CeO_x/Ti-PILC catalysts

From Fig. 3, it is known that the temperatures at which the NH₃ escaped from the surface were at 126.8°C, 153.9°C, and 153.9°C for Mn-CeO_x/Ti-PILC, (K)Mn-CeO_x/Ti-PILC, and (Ca)Mn-CeO_x/Ti-PILC, respectively. NH₃ release temperature over Mn-CeO_x/Ti-PILC was the lowest among the three catalysts. All the data proved that Mn-CeO_x/Ti-PILC adsorbed more NH₃ and NH₃ on its surface released more quickly than (K)Mn-CeO_x/Ti-PILC and (Ca)Mn-CeO_x/Ti-PILC. More amount of NH₃ on the surfaces of the catalysts helped to improve SCR activity, and easily escape of NH₃ might help improve the reaction of NH₃ with NO during SCR reaction, which was also help to SCR reaction. The higher SCR activity for (Ca)Mn-CeO_x/Ti-PILC than (K)Mn-CeO_x/Ti-PILC might be due to the more absorbed NH₃ with higher acidity on the surfaces of (Ca)Mn-CeO_x/Ti-PILC than (K)Mn-CeO_x/Ti-PILC.

3.3 Redox behaviors of the catalysts

It has been also established that the oxidative dehydrogenation of the adsorbed ammonia species by active components of catalysts is another key step in the SCR of NO by NH₃ [3,5], which is determined by the redox behaviors of the catalysts. The redox property of the catalysts can be measured by H₂-TPR. In the process of H₂-TPR, the metal oxides of the catalyst can be reduced by H₂ at various temperatures. By analyzing the reduction temperature, the redox property of the catalysts can be distinguished. To investigate the effects of doping K and Ca on the redox property of the catalysts, the H₂-TPR profiles for Mn-CeO_x/Ti-PILC, (K)Mn-CeO_x/Ti-PILC and (Ca)Mn-CeO_x/Ti-PILC are shown in Fig. 4. As shown by the profiles, a dominative consumption peak for H₂ at 354.4°C can be observed over the Mn-CeO_x/Ti-PILC sample. In comparison with Mn-CeO_x/Ti-PILC, the main feature of the TPR profile for (Ca)Mn-CeO_x/Ti-PILC was shifting from 354.4°C to higher temperature 385.0°C. The profile of (K)Mn-CeO_x/Ti-PILC was very different from those of Mn-CeO_x/Ti-PILC and (Ca)Mn-CeO_x/Ti-PILC. There were two distinct reduction peaks located at 359.9°C and 435.3°C, corresponding to the stepwise reduction of the mixed metal oxides on the surface of the catalyst. The average reduction peaks for (K)Mn-CeO_x/Ti-PILC were higher than those of (Ca)Mn-CeO_x/Ti-PILC and Mn-CeO_x/Ti-PILC. It is known that the reduction of pure MnO_x by H₂ has two peaks: the first peak at 353°C accounts for the reduction of MnO₂ and Mn₂O₃ to Mn₃O₄, while the second one at 456°C is attributed to the reduction process of Mn₃O₄ to MnO [14]. The reduction of Ce⁴⁺ to Ce³⁺ took place along with the reduction of manganese ions [15]. The large H₂ consumption peak had been observed for the catalysts might be corresponding to the overlap reduction of manganese oxides and cerous oxides on the surface of the catalysts. The fact of the H₂-TPR profiles shifting to higher temperatures indicated that with the introduction of

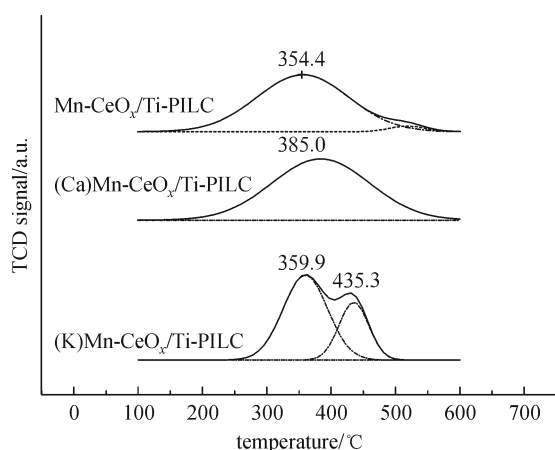


Fig. 4 H₂-TPR profiles for Mn-CeO_x/Ti-PILC, (K)Mn-CeO_x/Ti-PILC, and (Ca)Mn-CeO_x/Ti-PILC catalysts

K and Ca, the reducibility of the active ingredients on the surfaces of the catalysts have been suppressed, which meant that the redox properties of the catalysts have been suppressed. As stated before, the presences of alkali also significantly decreased the reduction of vanadia species for V₂O₅-WO₃/TiO₂, which led to the deactivation of the activity [16].

3.4 XPS analysis of the catalysts

XPS was used to understand the surface compositions of Mn, Ce and O on the catalysts. Two main peaks in Fig. 5 due to Mn 2p_{1/2} and Mn 2p_{3/2} were observed in Mn-CeO_x/Ti-PILC catalyst from 636 eV to 660 eV. After the peaks disassembling for Mn 2p_{2/3}, two small peaks centering at about 641.6 eV and 643.5 eV can be obtained, which indicated the co-existence of Mn³⁺ and Mn⁴⁺ on the surfaces of the catalysts. The peaks for Mn³⁺ and Mn⁴⁺ shifted to higher binding energy (BE) values at 641.9 eV and 643.9 eV for (Ca)Mn-CeO_x/Ti-PILC catalyst, and at 642.2 eV and 644.1 eV for (K)Mn-CeO_x/Ti-PILC catalyst. From Fig. 5, the ratio of Mn³⁺/Mn⁴⁺ were obtained at 1.16, 1.22 and 1.54 for (K)Mn-CeO_x/Ti-PILC, (Ca)Mn-CeO_x/Ti-PILC and Mn-CeO_x/Ti-PILC, which indicated that with the doping of K and Ca, more MnO₂ was present on the surfaces of the catalysts. It is known that the valence state of manganese is relative to the SCR catalytic activity. Kapteijn et al. [17] suggested that MnO₂ appeared to exhibit the highest activity, followed by Mn₅O₈, Mn₂O₃, Mn₃O₄ and MnO. Peña et al. [18] also thought that MnO₂ contributed to the high activity of Mn/TiO₂. The presence of K and Ca on the surfaces of the catalysts improved the percentage of Mn⁴⁺ but decreased SCR activity, which indicated that the effect of acidity and redox behaviors on the activity of the catalysts was more important than valence state of manganese in our studies. The intensity of Mn XPS for the catalysts was found to decrease with the doping of K and Ca in our studies (Fig. 5).

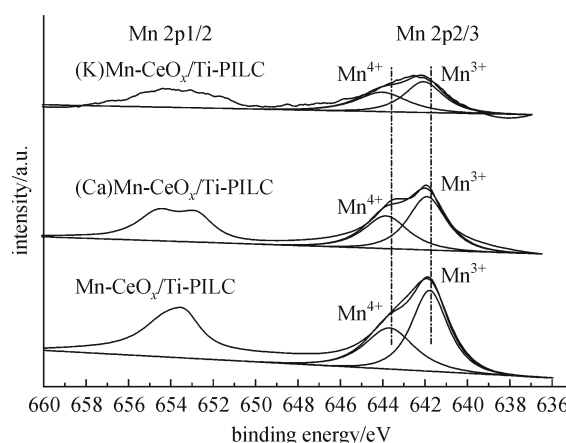


Fig. 5 Mn 2p XPS of the catalysts before and after the dopes of Ca and K

Ce 3d XPS spectra of the catalysts before and after dope of Ca and K were presented in Fig. 6. According to previous reports [19,20], XPS peaks denote as V (882.5 eV), V''(888.8 eV), V'''(898.4 eV), U (901.0 eV), U''(907.5 eV), and U'''(916.7 eV) were assigned to Ce⁴⁺ species while U₀ (898.8 eV), U'(903.5 eV), V₀ (880.3 eV), and V'(884.9 eV) were attributed to Ce³⁺ species. According to this result, tetravalent Ce⁴⁺ and trivalent Ce³⁺ were considered to coexist on the surface of the catalysts in our studies. Ce 3d XPS spectra for (Ca)Mn-CeO_x/Ti-PILC was almost similar but with little deviation to that of Mn-CeO_x/Ti-PILC. The Ce 3d XPS spectra for (K)Mn-CeO_x/Ti-PILC was very different from both of them. Ce3d XPS spectra for (K)Mn-CeO_x/Ti-PILC was not well detached and its intensity was much smaller than those of (Ca)Mn-CeO_x/Ti-PILC and Mn-CeO_x/Ti-PILC. The presence of K and Ca also restrained the intensity of XPS peaks for Ce³⁺ and Ce⁴⁺.

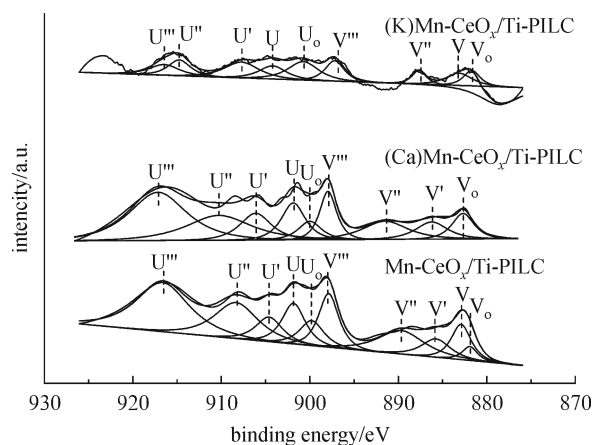


Fig. 6 Ce 3d XPS spectra of the catalysts before and after the dopes of Ca and K

It was suggested by Peña et al. [18] that the SCR reaction activity was relative to oxygen and hydroxyl groups linked to Mn. The XPS analysis for O element is also necessary in our studies. The XPS spectra for O1s (Fig. 7) showed that the O1s spectra had two distinct peaks. The peak at 529.6–530.0 eV corresponded to lattice oxygen (denoted as O_β) while the one at 531.3–531.7 eV corresponded to chemisorbed oxygen (denoted as O_α) [21]. The surface chemisorbed oxygen had also been reported to be helpful in the oxidation of NO to NO₂ [22], which was favorable to the reduction of NO in the SCR process. The ratios of O_α/O_β on the surfaces of Mn-CeO_x/Ti-PILC, (Ca)Mn-CeO_x/Ti-PILC, and (K)Mn-CeO_x/Ti-PILC were 1.43, 1.32, 1.28, respectively. The doping of K and Ca decreases the chemisorbed oxygen, which resulted in the decreasing of SCR activities. The presence of K and Ca also restrained the intensity of XPS peaks of O_α and O_β.

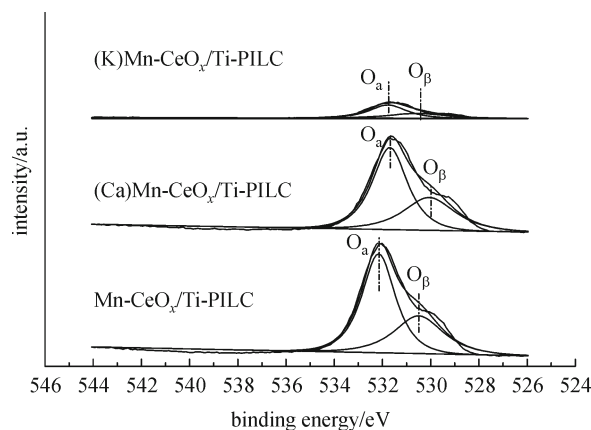


Fig. 7 O 1s XPS spectra of the catalysts before and after the dopes of Ca and K

4 Conclusions

K and Ca can poison the catalyst of Mn-CeO_x/Ti-PILC for selective catalytic reduction of NO with NH₃ at low temperature, and K exhibited more poisoning effect than Ca. With the dopes of K and Ca, the acidity, the redox property and chemisorbed oxygen on the surfaces of the catalysts were decreased, which resulted in a decreasing in SCR activity.

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