Research Article

The Poisoning Effect of Na Doping over Mn-Ce/TiO₂ Catalyst for Low-Temperature Selective Catalytic Reduction of NO by NH₃

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Sodium carbonate (Na₂CO₃), sodium nitrate (NaNO₃), and sodium chloride (NaCl) were chosen as the precursors to prepare the Na salts deposited Mn-Ce/TiO₂ catalysts through an impregnation method. The influence of Na on the performance of the Mn-Ce/TiO₂ catalyst for low-temperature selective catalytic reduction of NO_x by NH₃ was investigated. Experimental results showed that Na salts had negative effects on the activity of Mn-Ce/TiO₂ and the precursors of Na salts also affected the catalytic activity. The precursor Na₂CO₃ had a greater impact on the catalytic activity, while NaNO₃ had minimal effect. The characterization results indicated that the significant changes in physical and chemical properties of Mn-Ce/TiO₂ were observed after Na was doped on the catalysts. The significant decreases in surface areas and NH₃ adsorption amounts were observed after Na was doped on the catalysts, which could be considered as the main reasons for the deactivation of Na deposited Mn-Ce/TiO₂.

1. Introduction

The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with NH₃ is an effective process for cleaning NO_x from stationary sources [1]. Low-temperature SCR technology is a promising method to remove NO_x in flue gas because the unit can be placed downstream of the particle control device and desulfurization system, and the temperature at this point is below 160°C [2, 3]. Some researchers have recently reported that manganese-cerium (Mn-Ce) mixed oxides supported on TiO₂ catalysts showed high SCR activity and good SO₂ resistance at low temperature [4–7]. It has been found that the manganese oxides (MnO_x) contain various kinds of labile oxygen and the ceria (CeO₂) owns high oxygen storage and redox capacity, which are proved to be very active in catalyzing the NO reduction by NH₃ [8, 9]. And the TiO₂ as the supporter also can provide large surface area, high thermal stability, strong mechanical strength, and high sulfur resistance [10].

Although the low-temperature SCR unit is commonly arranged after particulate control device, there is still a small amount of dust which contains many physical and chemical

deactivating species such as alkali/alkaline earth metals in flue gas. It could reduce catalytic activity when the catalyst is exposed in this complex flue gas for long time [11, 12]. In addition, when the low-temperature SCR technology is used to remove the NO_x emission from some industrial furnace, such as cement kiln and glass kiln, the Mn-Ce/TiO₂ catalyst could be subjected to greater influence by deposition of alkali/alkaline earth metals [13, 14]. Therefore, it is valuable to investigate the effects of alkali/alkaline earth metals on Mn-Ce/TiO₂ for low-temperature SCR, which few researchers have concerned about. In this study, we try to investigate the impact of deposited sodium (Na) on the physical and chemical properties of Mn-Ce/TiO₂ catalysts. Sodium carbonate (Na₂CO₃), sodium nitrate (NaNO₃), and sodium chloride (NaCl) were chosen as the sodium-containing precursors to prepare the Na deposited Mn-Ce/TiO₂ catalysts.

2. Experimental

2.1. Catalyst Preparation. All chemicals used in this study were of analytical grade and were used without further purification. In this experiment, the molar ratio of Ce:Mn:Ti

was 0.07:0.4:1, which has been reported by Wu et al. [15] with high SCR activity. The Na deposited Mn-Ce/TiO₂ catalysts were prepared by impregnation of TiO₂ (Degussa P25) with Mn(NO₃)₂, Ce(NO₃)₃, and three kinds of sodium salts (Na₂CO₃, NaNO₃, and NaCl). 4.0 g TiO₂ powder was dispersed into 100 mL aqueous solution. Then 0.02 mol of Mn(NO₃)₂, 0.0035 mol of Ce(NO₃)₃, and a certain amount of Na salts were added into the solution. The loading amounts of sodium were 0.05, 0.1, 0.2, 0.5, 1, and 2 wt.%. The slurry was then stirred for 48 h. After that, it was heated at 105°C for 12 h. The solid samples were crushed and sieved to 60–100 mesh and then calcined at 400°C for 2 h in air. The Na₂CO₃, NaCl, and NaNO₃ deposited Mn-Ce/TiO₂ catalyst were denoted by Mn-Ce/TiO₂ (C), Mn-Ce/TiO₂ (Cl), and Mn-Ce/TiO₂ (N), respectively.

2.2. Catalyst Characterization. The structures of the samples were determined by X-ray diffraction patterns (XRD) obtained on a Bruker D8 Advance diffract meter. The surface areas of catalysts were calculated by using the Brunauer-Emmett-Teller (BET) method, with Micromeritics ASSP 2020 equipment by N₂ physisorption at 77 K. The surface atomic states of the catalysts were analyzed by X-ray photoelectron spectroscopy (XPS) with Thermo Escalab 250Xi. Transmission electron microscopy (TEM) images were examined by JEM 2010. Temperature programmed desorption (TPD) was carried out on a custom-made TCD setup in a conventional flow system at atmospheric pressure using 100 mg catalysts (40–60 mesh). After being pretreated in He at 400°C for 1 h, the samples were saturated with a stream of 4% NH₃ and He balance at a flow rate of 30 mL/min for 30 min. The NH₃ desorption was carried out by heating NH₃-adsorbed samples from 100 to 900°C at the rate of 5°C/min in He (30 mL/min).

2.3. Activity Tests. The SCR activity measurements were carried out in a fixed-bed reactor at 60–160°C containing 4 g catalyst with a gas hourly space velocity (GHSV) of 24,000 h⁻¹. The typical reactant gas consisted of 500 ppm NO, 500 ppm NH₃, 5 vol.% O₂, and balance N₂. NO, NO₂, and O₂ were measured by a flue gas analyzer (MRU Vario Plus, Germany). NH₃ was analyzed with a portable NH₃ analyzer (Nantong Water Environmental Protection Technology Co. Ltd., Model MOT 400).

3. Results and Discussion

3.1. Catalytic Activity. The activity of the prepared catalysts with the variation of temperature is presented in Figure 1. It can be seen from Figure 1(a) that the NO conversion of all samples increased with the increasing temperature. The Mn-Ce/TiO₂ catalyst showed high catalytic activity for the low-temperature SCR of NO with NH₃. Over 99% of NO conversion was obtained when the temperature reached 100°C. The SCR activities of 1% Mn-Ce/TiO₂ (C), Mn-Ce/TiO₂ (Cl), and Mn-Ce/TiO₂ (N) all declined when Na salts were deposited on the catalysts. Figure 1(a) also shows that the SCR activity decreased in the following sequence: Mn-Ce/TiO₂ > Mn-Ce/TiO₂ (N) > Mn-Ce/TiO₂ (Cl) > Mn-Ce/TiO₂ (C).

It is indicated that Na salts had a negative effect on the activity of Mn-Ce/TiO₂ and the precursors of Na also affected the catalytic activity. The precursor Na₂CO₃ had a greater impact on the catalytic activity, while NaNO₃ had minimal effect. The deposited NaNO₃ could decompose to NaNO₂ and O₂ after calcination at 400°C for 12 h, while Na₂CO₃ and NaCl could not decompose at 400°C. Therefore, the massive agglomeration of Na₂CO₃ and NaCl could block the micropores and covered the active sites, which is considered as the reason for the deactivation of Na doped Mn-Ce/TiO₂ catalyst [11]. The NO_x conversions of Mn-Ce/TiO₂ (C) and Mn-Ce/TiO₂ (N) were shown in the Figures 1(b) and 1(c). The catalytic activity of samples declined with the increasing amounts of Na doped from 0 to 2%. 2% Mn-Ce/TiO₂ (C) showed the lowest activity and only 17.8% of NO conversion was obtained at 160°C. The results demonstrated that the Mn-Ce/TiO₂ catalyst could be gradually deactivated as the loading amounts of Na salts increased.

3.2. Catalyst Microstructure. The XRD patterns of Na doped Mn-Ce/TiO₂ catalysts with different Na precursors were shown in Figure 2. For the undoped Mn-Ce/TiO₂ catalyst, the XRD pattern only existed as a mixing form of anatase and rutile [14]. And the peaks of manganese or cerium oxides were not detected, which indicated that manganese or cerium oxides were well dispersed on the TiO₂ carrier. After different Na salts were deposited, two extra peaks around 28.72° and 33.02° were detected. It has been reported that the two peaks were identified as Mn₃O₄ and Mn₂O₃ [14, 15]. The results implied that Na salts doping could induce the crystallization of MnO_x phases, which had adverse effect on catalytic activity due to the transformation of the amorphous manganese oxides to crystal phase [16]. On the other hand, the Mn-Ce/TiO₂ (N) catalyst had peaks of weak intensity for Mn₃O₄ and Mn₂O₃, which could be considered as one of the reasons that NaNO₃ had weaker impact on the deactivation of Mn-Ce/TiO₂ catalyst. In particular, for all Mn-Ce/TiO₂ samples, characteristic peaks of anatase and rutile with similar position, intensities, and widths were detected, which implied that the phase structure and the crystallite size of TiO₂ particles in as-prepared samples had no obvious changes after Na doping.

The morphology of 2% Mn-Ce/TiO₂ (C) catalyst was further investigated by TEM and HR-TEM images as shown in Figure 3. From the insert image of Figure 3, it can be seen that primary particles have the diameters predominantly ranged from 10 to 20 nm. From the HR-TEM image illustrated in Figure 3, four kinds of clear lattice fringes could be observed for 2% Mn-Ce/TiO₂ (C) catalyst. The spacing distances between the lattice planes of 0.352 nm and 0.32 nm matched with the anatase (101) phase and rutile (110) phase [17]. And the lattice fringes with lattice plane distances observed about 0.384 nm and 0.492 nm corresponded to Mn₂O₃ (211) and Mn₃O₄ (101) planes [14], which were in agreement with the information obtained from the XRD results.

The specific surface areas, pore volumes, and pore sizes of the Mn-Ce/TiO₂ catalysts prepared with different Na precursors are summarized in Table 1. Significant decreases

FIGURE 1: Variations of NO conversion efficiency with temperature for prepared Mn/Ce-TiO₂ catalysts. (a) Comparison of catalytic activity over the Na doped Mn-Ce/TiO₂ prepared by different Na precursors. (b) Comparison of catalytic activity over Mn-Ce/TiO₂ (C) with different Na doping amounts. (c) Comparison of catalytic activity over Mn-Ce/TiO₂ (N) with different Na doping amounts. Operating conditions: 500 ppm NO, 500 ppm NH₃, 5% O₂, and balance N₂, GHSV = 24,000 h⁻¹.

in surface areas and pore volumes were observed after Na deposited on the catalysts. This could be caused by the massive agglomeration of Mn-Ce/TiO₂ due to the Na salts deposited, which blocked the micropores in Mn-Ce/TiO₂ lattice and increased average pore size. It was also observed that the surface area and pore volume of Mn-Ce/TiO₂ (N) were larger than those of Mn-Ce/TiO₂ (Cl) and Mn-Ce/TiO₂ (C). It is indicated that the precursor NaNO₃ has little effect on pore structure of the catalyst. The variations in specific surface areas of catalysts were in good agreement with the catalytic activities. Mn-Ce/TiO₂ (N) with the larger specific surface area showed better SCR activity.

3.3. Catalyst Composition Analysis. In order to identify the states of surface species on the prepared catalysts, the samples were examined by XPS high-resolution scans over Ti 2p, Mn 2p, Ce 3d, O 1s, and Na 1s spectra regions. And the atomic compositions of Ti, Mn, Ce, and O on the surface are shown in Table 2.

The Ce 3d XPS spectra are presented in Figure 4(a). The XPS spectra revealed that Ce 3d orbit was composed of two multiplets (v and u). The peaks labeled u and v were due to 3d_{3/2} and 3d_{5/2} spin-orbit states, respectively. The u, u'', and u''' and v, v'', and v''' peaks were attributed to Ce⁴⁺ species,

FIGURE 2: XRD patterns of Na doped Mn-Ce/TiO₂ catalysts prepared by different Na precursors (□ TiO₂-anatase, ◆ TiO₂-rutile, ▽ Mn₃O₄, and ◇ Mn₂O₃).

FIGURE 3: TEM and HR-TEM images of 2% Mn-Ce/TiO₂ (C) sample.

TABLE 1: Physical properties of the catalysts prepared with different Na precursors.

Catalysts	BET surface area (m ² /g)	Pore volume (×10 ⁻² cm ³ /g)	Average pore diameter (nm)
Mn-Ce/TiO ₂	44.52	28.39	25.51
2% Mn-Ce/TiO ₂ (C)	31.48	22.04	30.85
2% Mn-Ce/TiO ₂ (Cl)	32.42	25.65	31.64
2% Mn-Ce/TiO ₂ (N)	36.58	27.58	28.61

while u' and v' were assigned to Ce³⁺ species [15]. No obvious difference was observed from the Ce 3d XPS spectra for Mn-Ce/TiO₂ and Na doped Mn-Ce/TiO₂ samples.

As shown in Figure 4(b), the Mn 2p region consists of a spin-orbit doublet with Mn 2p_{1/2} having binding energy of about 653 eV and Mn 2p_{3/2} with binding energy of 642 eV,

TABLE 2: Surface atomic concentrations of Mn-Ce/TiO₂ catalysts with different sodium oxides.

Catalysts	Surface atomic concentrations (%)			
	Mn	Ti	Ce	O
Mn-Ce/TiO ₂	8.32	26.5	3.23	61.95
2% Mn-Ce/TiO ₂ (C)	3.57	24.77	1.56	42.14
2% Mn-Ce/TiO ₂ (Cl)	4.59	15.43	1.44	66.82
2% Mn-Ce/TiO ₂ (N)	7.17	25.7	2.97	58.9

which are characteristic of a mixed-valence manganese system [18, 19]. The Mn 2p_{3/2} spectra could be split into three peaks at binding energy of 642.8, 641.2, and 646.5 eV, which were ascribed to Mn⁴⁺, Mn³⁺, and Mn-nitrate, respectively [20, 21]. For undoped Mn-Ce/TiO₂, the Mn-nitrate could be originated from Mn(NO₃)₂, as one of the precursors for the preparation of Mn-Ce/TiO₂. It can be clearly seen from Figure 4(a) that the atomic concentration of Mn-nitrate on Mn-Ce/TiO₂ (N) is much higher than that on undoped Mn-Ce/TiO₂, which may be attributed to the decomposition of Mn(NO₃)₂ restrained with the Na salts doping. The decrease of Mn³⁺ and Mn⁴⁺ on Na salts deposited Mn-Ce/TiO₂ could be considered as one of the reasons for the decrease of catalyst activity [22].

3.4. NH₃-TPD Analysis. The surface acidity properties of the catalysts were analyzed by NH₃-TPD. The NH₃-TPD curves of Mn-Ce/TiO₂ and 2% Mn-Ce/TiO₂ (N) are shown in Figure 5. As shown in Figure 5, one broad peak spanned in the temperature range of 100–300°C was observed for both samples, attributed to NH₃ desorbed by weak and medium acid sites. For undoped Mn-Ce/TiO₂, the desorption peaks centered at 552 and 663°C could be ascribed to the nature of Brønsted acid and Lewis acid, respectively [23]. At the temperature around 743°C, the strong peak observed was probably due to the N₂ desorption [24]. The shape of the NH₃-TPD curve obtained from 2% Mn-Ce/TiO₂ (N) was very different. The peak at 670°C disappeared, while the peak of N₂ desorption increased greatly. It is indicated that the Lewis acid sites of Mn-Ce/TiO₂ were reduced after Na salts were deposited. It is known that the strong acidity on catalyst could play an important role in the adsorption capacity of NH₃ for the sample [25]. The decrease of Lewis acid sites could be considered as the main factor for decrease of NH₃ adsorption amount on Na deposited Mn-Ce/TiO₂.

4. Conclusions

The catalytic activity experiments showed that Na salts had strong poisoning influence on Mn-Ce/TiO₂ catalyst, which seriously reduced the low-temperature SCR activity. The precursor Na₂CO₃ had more negative impact on the catalytic activity, while NaNO₃ had minimal effect. XPS results indicated that the atomic content of Mn³⁺ and Mn⁴⁺ on catalyst surface could decrease with the addition of Na. BET and NH₃-TPD results showed that the significant decreases in surface areas and NH₃ adsorption amounts were observed

FIGURE 4: XPS high-resolution scans over (a) Ce 3d and (b) Mn 2p peaks on (1) Mn-Ce/TiO₂ and (2) 2% Mn-Ce/TiO₂ (N) catalyst.

FIGURE 5: NH₃-TPD profiles for Mn-Ce/TiO₂ catalysts prepared with different Na precursors, (1) Mn-Ce/TiO₂ and (2) 2% Mn-Ce/TiO₂ (N).

after Na salts were deposited on the catalysts, which could be considered as the main reasons for the deactivation of Na doped Mn-Ce/TiO₂.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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