铈改性钛基层柱粘土负载锰催化剂上低温 NH_3 选择性催化还原 NO沈伯雄^{1,*}, 姚燕¹, 马宏卿¹, 刘亭²¹ 南开大学环境科学与工程学院, 天津 300071² 中国石化青岛安全工程研究院, 山东青岛 266071

摘要: 采用离子交换法制备了钛基层柱粘土 ($\text{TiO}_2\text{-PILC}$), 并应用浸渍法将 Mn 负载于其上制得不同 Mn 含量的 $x\text{Mn}/\text{TiO}_2\text{-PILCs}$ 催化剂, 考察了催化剂低温 NH_3 选择性催化还原 NO ($\text{NH}_3\text{-SCR}$) 活性, 研究了添加 Ce 对 $8\%\text{Mn}/\text{TiO}_2\text{-PILC}$ 催化剂活性及其抗水蒸气抗 SO_2 特性的影响。结果发现, $\text{TiO}_2\text{-PILC}$ 负载的锰基催化剂具有良好的抗水蒸气性能, 但在水蒸气和 SO_2 共存时失活严重。Ce 的添加对催化剂活性以及抗 SO_2 能力均有所提高, 其中 $8\%\text{Mn}\text{-}2\%\text{Ce}/\text{TiO}_2\text{-PILC}$ 在 $200\text{ }^\circ\text{C}$ 时 NO 去除率达到 95%, 同时 SO_2 失活速率明显比其他催化剂低。采用 N_2 吸附-脱附、X 射线衍射、 NH_3 程序升温脱附、 H_2 程序升温还原和 X 射线光电子能谱等技术对催化剂结构和性质进行了表征。结果表明, 所制备催化剂具有丰富的中孔结构和较大的比表面积; Ce 的添加使 Mn 在催化剂表面分散性更好, 提高了催化剂表面酸性和催化剂氧化还原性能, 从而使其活性和抗硫性能增加。

关键词: 低温选择性催化还原; 钛基层柱粘土; 氧化锰; 氧化铈; 中毒

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*通讯联系人. 电话: (022)23503219; 传真: (022)23508807; 电子信箱: shenbx@nankai.edu.cn

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Ceria Modified $\text{MnO}_x/\text{TiO}_2\text{-Pillared Clays Catalysts for Selective Catalytic Reduction of NO with } \text{NH}_3 \text{ at Low Temperature}$ SHEN Boxiong^{1,*}, YAO Yan¹, MA Hongqing¹, LIU Ting²¹ College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China² Sinopec Research Institute of Safety Engineering, Qingdao 266071, Shandong, China

Abstract: Titania-pillared clays ($\text{TiO}_2\text{-PILC}$) were synthesized by ion exchange and manganese was introduced as the active phase. The catalytic behavior of the $x\text{Mn}/\text{TiO}_2\text{-PILC}$ catalysts was studied for the low-temperature selective catalytic reduction (SCR) of NO with NH_3 . A series of Ce-doped $8\%\text{Mn}\text{-}y\text{Ce}/\text{TiO}_2\text{-PILC}$ catalysts were prepared and evaluated for their performance in the low-temperature SCR of NO with NH_3 , their resistance to water vapor (H_2O), and their resistance to sulfur dioxide (SO_2). It was found that the NO conversion properties of the $8\%\text{Mn}/\text{TiO}_2\text{-PILC}$ catalysts could be significantly improved by adding Ce and all the catalysts gave high resistance to H_2O but were sensitive to SO_2 . The catalyst with a Ce loading of 2% gave 95% NO conversion at $220\text{ }^\circ\text{C}$ and exhibited a moderate SO_2 -poisoning resistance compared with the other catalysts. X-ray diffraction, N_2 adsorption-desorption, temperature-programmed desorption of NH_3 , X-ray photoelectron spectroscopy, and temperature-programmed reduction of H_2 were used to characterize the properties of the catalysts. The addition of Ce improved the diffusion of Mn on the surfaces of the catalysts, which enhanced the surface acidity and improved the reduction properties of the catalysts and these were the main influencing factors for the low-temperature SCR.

Key words: low-temperature selective catalytic reduction; titania-pillared interlayered clay; manganese oxide; cerium; poisoning

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*Corresponding author. Tel: +86-22-23503219; Fax: +86-22-23508807; E-mail: shenbx@nankai.edu.cn

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The selective catalytic reduction (SCR) of NO with NH_3 is an efficient technology for NO removal from flue gas for a fixed combustion system [1–3]. Because of the multivalent nature of manganese, manganese oxides have been studied extensively as catalysts for the low temperature SCR of NO with NH_3 [4–7]. Upon doping MnO_x -based catalysts with Fe and Cu a reaction with Mn and an interaction between the mixed oxides influences the oxidative ability of the manganese species, the oxidative ability of the manganese species and the surface structure, which enhances catalytic properties during low temperature SCR [8–10]. Ceria (CeO_2), as a good oxygen reservoir, has attracted considerable interest because of its oxygen storage and redox properties [11–13]. Wu et al. [14] prepared ceria modified $\text{MnO}_x/\text{TiO}_2$ and found that the introduction of Ce improved the oxygen mobility and the NH_3 chemisorption ability of the catalysts resulting in improved SCR activity. The resistance to SO_2 was found to be greatly enhanced for Ce modified MnO_x -based catalysts during low temperature SCR [15]. Additionally, $\text{MnO}_x\text{-CeO}_2$ has been found to have high activity with 90%–100% selectivity for N_2 during the low temperature SCR of NO with NH_3 [4,6,16].

Catalyst supports are also believed to be important for SCR performance as they possess high surface areas, good thermal stability, and high active substance dispersion on surfaces [17,18]. Peña et al. [19] investigated NO conversion over TiO_2 -supported manganese oxides and concluded that metal-support interactions determined the redox properties of the catalyst and its SCR activity. Jin et al. [20] loaded Mn-Ce oxides onto TiO_2 and Al_2O_3 and found that carriers play an important role in NO conversion as they provide different acid sites and reaction pathways for the reaction.

Pillared interlayered clays (PILC) are two-dimensional zeolite-like materials, and are of interest because of their adjustable pore size distribution, their high thermal stability, and their low cost [21,22]. The use of PILC in the SCR of NO by NH_3 from 250 to 450 °C has been studied. Yang et al. [22] synthesized and tested the following five pillared clays based catalysts: Cr_2O_3 -PILC, Fe_2O_3 -PILC, TiO_2 -PILC, ZrO_2 -PILC, and Al_2O_3 -PILC for the SCR reaction. They found that pillared clays are a promising class of catalysts for SCR applications because they have high N_2 selectivity between 250 and 450 °C. Cheng et al. [23] reported that the $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3/\text{TiO}_2$ -PILC catalyst has higher activity and higher N_2 selectivity than commercial $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts, even in the presence of H_2O and SO_2 in flue gas. Chmielarz et al. [24] found that the introduction of copper into Ti- or Al-pillared montmorillonites showed high activities during DeNO_x process between 250 and 450 °C.

Despite the fact that pillared clays based materials have been extensively studied for the SCR of NO with NH_3 from 250 to 450 °C, few studies have been carried out on these

materials for the low temperature SCR [25]. In this paper, catalysts consisting of Mn-supported Ti-pillared clays with Ce modification were prepared and tested for the low temperature SCR of NO with NH_3 .

1 Experimental

1.1 Synthesis of the catalysts

Purified bentonite (Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China) was used as the raw material. The bentonite was dispersed in a beaker containing a water-acetone mixture as the solvent to create a suspended slurry. The clay slurry was stirred for 24 h at room temperature. A titanium pillaring solution was obtained by slowly adding tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) to 5.0 mol/L HCl at a H/Ti mol ratio of 2.0. The solution was stirred for 30 min and then aged for 3 h at room temperature. The obtained oligomeric solution was added dropwise into a suspension of the clay with vigorous stirring. The resulting solution containing 15 mmol of Ti per gram of clay was stirred for another 6 h and aged over 12 h at room temperature. After that, the solid fraction was separated by centrifugation and washed several times with distilled water until the liquid phase was chloride-free. The obtained samples were then dried at 80 °C to obtain the TiO_2 -PILC catalysts.

Manganese oxides were introduced by the incipient wetness impregnation of TiO_2 -PILCs with a proper amount of $\text{Mn}(\text{NO}_3)_2$. The obtained materials were then dried at 80 °C for 12 h and calcined in air at 550 °C for 6 h. The catalysts are denoted $x\text{Mn}/\text{TiO}_2$ -PILC. The cerium-added samples were obtained by incipient wetness impregnation by adding $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to the $\text{Mn}(\text{NO}_3)_2$ aqueous solution. Subsequent drying and calcination were carried out as for the $x\text{Mn}/\text{TiO}_2$ -PILC catalysts. The final Ce-doped catalysts are referred to as $x\text{Mn-yCe}/\text{TiO}_2$ -PILCs catalysts where x and y represent the mass ratio of Mn and Ce on the support, respectively.

1.2 Characterization of the catalysts

The textural parameters of the samples were determined by N_2 sorption at –196 °C using a NOVA 2000 automated gas sorption system (Quantachrome Instruments, USA). The specific surface area, pore volume, and pore size distribution of the catalysts were determined by BET or BJH methods.

The crystal structures of the samples were determined by X-ray diffraction (XRD) using a D/Max-2500 diffractometer (Rigaku Co., Japan) with monochromatized $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15405 \text{ nm}$). A broad scan analysis was carried out

in the 2θ range from 3° to 80° at a scan speed of $4\text{--}8^\circ/\text{min}$.

The total acidity and the acid distribution of the catalysts were measured by the temperature-programmed desorption (TPD) of NH_3 on a TP5080 with a TCD detector (xq-instrument, Tianjin, China). About 0.1 g sample (sieved to 0.2–0.3 mm) was inserted into a fixed-bed flow reactor using nitrogen as the flow gas. The samples were pretreated for 30 min at 550°C and then cooled to room temperature. The introduction of NH_3 was carried out over 30 min followed by a purge with nitrogen to remove the physically adsorbed NH_3 on the catalyst surface. Desorption under nitrogen was then carried out at $100\text{--}500^\circ\text{C}$ with a heating rate of $10^\circ\text{C}/\text{min}$.

The temperature-programmed reduction (TPR) of H_2 experiments were also carried out on the TP5080. The samples (0.1 g) were loaded and pretreated at 550°C in an atmosphere of N_2 and the samples cooled to room temperature. After that, the samples were reduced by $5\%\text{H}_2\text{--}95\%\text{N}_2$ at a flow rate of 30 ml/min from room temperature to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$.

X-ray photoelectron spectroscopy (XPS) was used to determine the surface atomic state of the catalysts using a Kratos Axis Ultra DLD spectrometer equipped with monochromated Al K_α radiation (1486.6 eV, Shimadzu Corporation, Japan). Charging of the catalyst samples was corrected by the binding energy of C 1s (284.6 eV) as an internal reference. The operating pressure was determined at room temperature and at a pressure of 1×10^{-7} Pa.

1.3 Catalytic activities

The SCR catalytic experiments were performed at atmospheric pressure in a fixed-bed stainless steel flow reactor (i.d. 1 cm) [26]. The temperature of the reactor was monitored and controlled by thermocouples that were inserted into the center of the catalyst bed. The reactant gases were fed to the reactor by an electronic mass flow controller. The composition of the initial gas mixture with a flux of 300 ml/min was as follows: NO 0.06 vol%, NH_3 0.06 vol%, O_2 3 vol%, H_2O 3 vol% (when used) SO_2 0.01 vol% (when used) and pure N_2 as balance. The NH_3 -SCR experiments were performed over 0.5 g catalyst (60–80 mesh) from 80 to 240°C and the gas hourly space velocity (GHSV) was 50000 h^{-1} .

NO from the reactor was analyzed using a flue gas analyzer (KM900; Kane International Ltd.). NO conversion was calculated as follows:

$$\text{NO conversion} = (\text{NO}_{\text{in}} - \text{NO}_{\text{out}}) / \text{NO}_{\text{in}} \times 100\%$$

where NO_{in} is the NO concentration of the reactor inlet, and NO_{out} is the NO concentration of the exit of the reactor.

2 Results and discussion

2.1 Catalytic performance of the $x\text{Mn}/\text{TiO}_2\text{-PILCs}$ catalysts

The $x\text{Mn}/\text{TiO}_2\text{-PILC}$ catalysts with different Mn loadings were evaluated for the SCR of NO using NH_3 as a function of temperature. The results are shown in Fig. 1. Only 15% NO conversion was obtained over the pure $\text{TiO}_2\text{-PILC}$ at 240°C . The addition of manganese to the $\text{TiO}_2\text{-PILC}$ increased the NO conversion greatly and this depended on the amount of Mn. The $2\%\text{Mn}/\text{TiO}_2\text{-PILC}$ catalyst gave a small increase in SCR activity from 180 to 240°C . There was an obviously variation in NO conversion with an increase in Mn content from 4% to 10% and the best activity was obtained over the $8\%\text{Mn}/\text{TiO}_2\text{-PILC}$ catalyst, which gave nearly 100% conversion at 220°C . However, NO conversion decreased with a further increase in the Mn content from 8% to 10%. The SCR activity decreased as follows: $8\%\text{Mn}/\text{TiO}_2\text{-PILC} > 6\%\text{Mn}/\text{TiO}_2\text{-PILC} \approx 10\%\text{Mn}/\text{TiO}_2\text{-PILC} > 4\%\text{Mn}/\text{TiO}_2\text{-PILC} > 2\%\text{Mn}/\text{TiO}_2\text{-PILC} > \text{TiO}_2\text{-PILC}$. By a comparison of the activities of the 8%Mn supported on the Ti-pillared clays with that on un-pillared clays we found that the 8%Mn/PILC catalyst only gave 37% NO conversion at 220°C , which is much lower than that of the $8\%\text{Mn}/\text{TiO}_2\text{-PILC}$ catalyst. The intercalation of Ti with the clays is thus necessary for low temperature SCR support.

Moreover, temperature plays a vital role in the activity of the catalysts, as reported in previous studies [11,27]. According to the results shown in Fig. 1, NO conversion remained mostly constant below 20% for all the catalysts from 80 to 120°C while a sharply increase in NO conversion was found with an increase in temperature from 120 to 240°C .

Fig. 1. Effect of manganese loading on NO conversion over the $x\text{Mn}/\text{TiO}_2\text{-PILC}$ catalysts. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 0.06\text{ vol}\%$, $[\text{O}_2] = 3\text{ vol}\%$, N_2 balance, total flow rate 300 ml/min.

2.2 Promoting effect of cerium

Since the 8%Mn/TiO₂-PILC catalyst was found to be an optimal SCR catalyst the promoting effects of ceria (CeO₂) on the SCR activities were studied over the 8%Mn/TiO₂-PILC catalyst. The NO conversion in the SCR reaction over the 8%Mn- γ Ce/TiO₂-PILC catalysts with different cerium loadings is shown in Fig. 2.

Fig. 2. Promoting effect of CeO₂ on the SCR activity of NO with NH₃ over the 8%Mn- γ Ce/TiO₂-PILC catalysts. Reaction conditions: [NO] = [NH₃] = 0.06 vol%, [O₂] = 3 vol%, N₂ balance, total flow rate 300 ml/min.

NO conversion for the 8%Mn- γ Ce/TiO₂-PILCs catalysts increased continuously with an increase in the reaction temperature. All the samples gave 90% NO conversion at 220 °C. Figure 2 shows that the SCR activity decreased as follows: 8%Mn-2%Ce/TiO₂-PILC > 8%Mn-1%Ce/TiO₂-PILC > 8%Mn-4%Ce/TiO₂-PILC > 8%Mn/TiO₂-PILC > 8%Mn-6%Ce/TiO₂-PILC. It is clear that at a Ce loading of 2% the catalyst gives superior NO reduction activity while at a Ce loading of more than 2% the NO conversion decreases. These results are in good agreement with previous studies [14,28]. It is reasonable to speculate that there is an optimal ceria content beyond which the overloaded Ce would cover the active sites and thus improvements to the SCR reaction would be small or even negative.

2.3 Characterization results of the catalysts

2.3.1 BET surface area and pore diameter analysis

The BET surface areas (A_{BET}), pore volumes (V_p), and average pore diameters (D_p) of three selected 8%Mn- γ Ce/TiO₂-PILC (γ = 0, 2%, and 6%) catalysts are summarized in Table 1. The BET surface area and pore volume of the 8%Mn/TiO₂-PILC catalyst are 133.7 m²/g and 0.1319 cm³/g, respectively. With an increase in Ce loading the BET and

the pore volumes of the 8%Mn- γ Ce/TiO₂-PILC catalysts decreased slightly. This might be a consequence of partially blocked pores because of the addition of ceria [29]. The catalysts are dominated by mesopores and they have a small ratio of micropores as determined by the t -plot method.

Table 1 Pore structure parameters of the 8%Mn- γ Ce/TiO₂-PILC samples

Sample	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_p/(\text{cm}^3/\text{g})$		D_p/nm
		Micro	Meso	
8%Mn/TiO ₂ -PILC	133.7	0.0163	0.1156	3.943
8%Mn-2%Ce/TiO ₂ -PILC	125.6	0.0193	0.1053	3.968
8%Mn-6%Ce/TiO ₂ -PILC	117.3	0.0140	0.1031	3.992

Figure 3(a) shows N₂ adsorption-desorption isotherms of the selected catalysts at -196 °C. For the 8%Mn/TiO₂-PILC catalysts the isotherms closely resemble type II and type IV isotherms (according to IUPAC), which indicates the existence of mesoporous pores in the sample. In addition, the hysteresis loop is of the H3 type implying that the catalysts have typical slit-like pores. This fact is consistent with their pore size distributions (Fig. 3(b)). For the 8%Mn-2%Ce/TiO₂-PILC and 8%Mn-6%Ce/TiO₂-PILC samples the isotherms are equivalent to that of the 8%Mn/TiO₂-PILC catalyst. The three catalysts have similar pore distributions with pore diameters of about 3.9 nm.

Fig. 3. Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) for the 8%Mn- γ Ce/TiO₂-PILC samples. (1) 8%Mn/TiO₂-PILC; (2) 8%Mn-2%Ce/TiO₂-PILC; (3) 8%Mn-6%Ce/TiO₂-PILC.

2.3.2 XRD

XRD spectra of purified bentonite, the TiO_2 -PILC, the 8%Mn/ TiO_2 -PILC catalyst, and the 8%Mn- γ Ce/ TiO_2 -PILC catalysts are shown in Fig. 4. As indicated in Fig. 4 the reflection of the basal (001) at 7.16° is obvious for the PILC sample and the two-dimensional hk reflections are present at 2θ angles of 19.8° and 34.9° . The peaks at 26.6° and 28° are reflections of quartz and cristobalite impurities in the clay [28,30,31]. Typical clay diffractions were also found for the TiO_2 -PILC except for the (001) reflection, as was reported for the delaminated TiO_2 -PILC [32,33]. No reflections of TiO_2 phases were present. The addition of Mn did not result in a change in the positions or shapes of the typical diffractions of the Ti-pillared clay but a decrease in intensity was observed as the Mn content increased. This implies that Mn and the TiO_2 -PILC may be in intimate contact and the interaction significantly influences the structure of the TiO_2 -PILC.

Fig. 4. XRD patterns of the 8%Mn/ TiO_2 -PILC and 8%Mn- γ Ce/ TiO_2 -PILC catalysts with different Ce loadings.

As for the 8%Mn/ TiO_2 -PILC catalyst, diffraction peaks attributed to crystalline Mn_2O_3 and MnO_2 were identified. After the addition of cerium oxide the diffraction peaks of Mn_2O_3 at $2\theta = 32.8^\circ$, 38.25° , and 55.24° became smaller and practically disappeared at a Ce content of 4%. Peaks for the crystalline CeO_2 phase were not found in any of the 8%Mn- γ Ce/ TiO_2 -PILC catalysts. This indicates that CeO_2 was amorphous and the presence of ceria led to a better dispersion of manganese on the TiO_2 -PILC. Strong intimate interactions therefore exist between manganese and ceria,

which inhibits crystallization for both species. As reported previously, amorphous MnO_x gives good performance for the SCR of NO with NH_3 while the crystalline phase contributes little to the SCR reaction [4,17,27,34].

2.3.3 NH_3 -TPD

The adsorption abilities of NH_3 over the 8%Mn/ TiO_2 -PILC and 8%Mn- γ Ce/ TiO_2 -PILC catalysts were probed by NH_3 -TPD and their profiles are shown in Fig. 5. A sharp NH_3 desorption peak is present at about 160°C for all the catalysts. Additionally, a weak NH_3 desorption peak at 450°C appeared for the 8%Mn-1%Ce/ TiO_2 -PILC, 8%Mn-2%Ce/ TiO_2 -PILC and 8%Mn-6%Ce/ TiO_2 -PILC catalysts. The peak at about 160°C is considered to arise from the desorption of ammonia that was bound to the weak Brönsted acid sites while the NH_3 desorption at high temperature was due to NH_3 that desorbed from the Lewis centers [35]. The addition of Ce introduced some Lewis type centers, which are much stronger than Brönsted acid sites. This is a possible reason for the higher activity of the Ce-doped catalyst. The adsorption capacity of NH_3 on the catalyst surface is believed to be crucial for the SCR reaction [36,37]. The total amount of NH_3 that was desorbed decreases as follows: 8%Mn-2%Ce/ TiO_2 -PILC > 8%Mn-1%Ce/ TiO_2 -PILC > 8%Mn-4%Ce/ TiO_2 -PILC $\approx$ 8%Mn/ TiO_2 -PILC > 8%Mn-6%Ce/ TiO_2 -PILC. The surface acidities of the 8%Mn- γ Ce/ TiO_2 -PILCs catalysts increased upon loading with small amounts of Ce while the acidities of the catalysts decreased with a high Ce loading. The adsorption properties of NH_3 over the tested catalysts correlate well with their catalytic activities in the SCR reaction.

Fig. 5. NH_3 -TPD profiles of the 8%Mn/ TiO_2 -PILC and the 8%Mn- γ Ce/ TiO_2 -PILC catalysts.

2.3.4 H_2 -TPR

Figure 6 shows the H_2 -TPR profiles of the TiO_2 -PILCs,

Fig. 6. H_2 -TPR profiles of the TiO_2 -PILCs, 8%Mn/ TiO_2 -PILC, and 8%Mn- y Ce/ TiO_2 -PILC catalysts.

8%Mn/ TiO_2 -PILC, and 8%Mn- y Ce/ TiO_2 -PILC catalysts. The TiO_2 -PILCs showed no obvious H_2 consumption peak over the whole temperature range, as shown in Fig. 6. Therefore, all the H_2 consumption peaks for the 8%Mn/ TiO_2 -PILC were due to the reduction of manganese species. The H_2 -TPR profile of the 8%Mn/ TiO_2 -PILC was characterized by two overlapping reduction peaks at 422 and 486 °C. Although there are many similarities such as the preparation method, the support, and the H_2 test conditions during the reduction of the active phase in qualitative and quantitative terms [38], similar properties were found for the MnO_x -loaded catalysts. The two-step reduction process on the 8%Mn/ TiO_2 -PILC can be broken down as follows [14,39,40]: the first reduction peak at 422 °C corresponds to the reduction of $\text{MnO}_2/\text{Mn}_2\text{O}_3$ to Mn_3O_4 and the other peak at 486 °C is due to the reduction of Mn_3O_4 to MnO .

Compared with the 8%Mn/ TiO_2 -PILC the reduction features of the 8%Mn- y Ce/ TiO_2 -PILC were dramatically modified because of the addition of Ce. Tang et al. [41] previously stated that the addition of ceria to manganese oxide accelerated the mobility of the surface oxygen species and led to an easier reduction of manganese oxide. It is interesting to note that for the 8%Mn- y Ce/ TiO_2 -PILC catalysts the temperature of the first peak at 422 °C gradually shifted to lower temperatures until a loading of 2%, and when the Ce loading was higher than 2% the first reduction peaks shifted back to higher temperature. This means that the reduction ability at low temperature increased for Ce loadings less than 2% and then decreased as more ceria oxides species were added. Similar reduction characteristics were also observed over the Ce modified $\text{MnO}_x/\text{TiO}_2$ catalysts by Wu et al. [14]. Moreover, with an increase in ceria content the temperature of the first reduction peak increased and over-

lapped with the second reduction peak at 400 °C for the 8%Mn-6%Ce/ TiO_2 -PILC catalyst. It has been reported that the redox abilities of the catalysts influence their catalytic activity [41]. In our experiments, changes in the reduction properties at low temperature for the 8%Mn- y Ce/ TiO_2 -PILC catalysts were consistent with their SCR activities.

CeO_2 has two reduction peaks at about 500 and 800 °C because of the reduction of surface and bulk oxygen in CeO_2 , respectively [43]. For the studied 8%Mn- y Ce/ TiO_2 -PILC catalysts no independent reduction peaks attributable to CeO_2 were observed. This illustrates the good interaction between cerium and manganese in the Ce-added catalysts. Therefore, the single reduction peak at 400 °C for the 8%Mn- y Ce/ TiO_2 -PILC mainly corresponds to the reduction of $\text{MnO}_2/\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$ and the surface reduction of $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ may also be included in this process. Delimaris et al. [40] proposed that the reduction of Ce^{4+} to Ce^{3+} can take place with the reduction of manganese ions during the H_2 -TPR of the MnO_x - CeO_2 catalysts that were prepared by a urea combustion method.

2.3.5 XPS

The surface elemental concentrations for the 8%Mn/ TiO_2 -PILC and 8%Mn- y Ce/ TiO_2 -PILC ($y = 2\%$ and 6%) catalysts are shown in Table 2. The photoelectron peaks of Mn $2p$, Ce $3d$, and O $1s$ are shown in Fig. 7. For the three samples, two main peaks due to Mn $2p_{3/2}$ and Mn $2p_{1/2}$ are present between 636 to 660 eV. The binding energies of Mn $2p_{3/2}$ and Mn $2p_{1/2}$ indicate a mixed-valence manganese system (Mn^{3+} and Mn^{4+}) [14,26], which agrees with the above XRD results. As shown in Table 2, no Ce is present on the surface of 8%Mn-2%Ce/ TiO_2 -PILC indicating that Ce is preferentially well dispersed on the surface of the catalysts, as shown by XRD. The Ce $3d$ XPS spectra of the 8%Mn-6%Ce/ TiO_2 -PILC catalyst gave six features of Ce^{4+} ($\text{U}+\text{U}''+\text{U}''' + \text{V}'''+\text{V}''+\text{V}$) and two features of Ce^{3+} ($\text{U}'+\text{V}'$), as shown in Fig. 7(b) [14,44]. These results confirm that Ce^{4+} and Ce^{3+} coexist on the surface of the catalysts and that the Ce^{4+} oxidation state is dominant.

The XPS spectra for O $1s$ shows that two distinct peaks are present on the catalysts investigated [40]. The O $1s$ XPS spectra show a main peak at a binding energy of 529.6–530.0 eV and this is assigned to lattice oxygen (denoted O β) from the metal oxides. The peak at 531.5–532.7

Table 2 Elemental concentrations on the surface of the catalysts

Sample	Surface elemental concentration (%)			
	Ce	Mn	O α	O β
8%Mn/ TiO_2 -PILC	—	7.82	63.31	8.57
8%Mn-2%Ce/ TiO_2 -PILC	—	6.72	77.10	2.56
8%Mn-6%Ce/ TiO_2 -PILC	0.86	6.99	57.70	12.23

Fig. 7. Mn 2p (a), Ce 3d (b), and O 1s (c) XPS spectra of the 8%Mn- y Ce/TiO₂-PILC samples. (1) 8%Mn/TiO₂-PILC; (2) 8%Mn-2%Ce/TiO₂-PILC; (3) 8%Mn-6%Ce/TiO₂-PILC.

eV corresponds to chemisorbed oxygen on the surface of the catalysts (donated O α). The surface chemisorbed oxygen has been reported to favor the reduction of NO during the SCR process [44]. Table 2 and Fig. 7 indicates that the 8%Mn-2%Ce/TiO₂-PILC catalyst with the highest chemisorbed oxygen has better NO conversion compared with the other catalysts.

2.4 Activity of the catalysts in the presence of H₂O and SO₂

Since water vapor and/or SO₂ are intrinsic components of flue gas, it is necessary to study the activities of the catalysts in the presence of H₂O and/or SO₂ at low temperature. Figure 8(a) illustrates the effect of H₂O on NO conversion

Fig. 8. Effect of H₂O on NO conversion over the 8%Mn/TiO₂-PILC and 8%Mn- y Ce/TiO₂-PILC catalysts. Reaction conditions: [NO] = [NH₃] = 0.06 vol%, [O₂] = 3 vol%, N₂ balance, total flow rate 300 ml/min.

over the 8%Mn/TiO₂-PILC and 8%Mn- y Ce/TiO₂-PILC catalysts at different reaction temperatures. For the three catalysts the conversion of NO remained constant during the test time indicating that the catalysts, based on the TiO₂-PILC gave good resistance to H₂O at 200 °C. The effects of H₂O on NO conversion over the 8%Mn-2%Ce/TiO₂-PILC catalyst at different temperatures was also studied and is shown in Fig. 8(b). When 3 vol% H₂O was introduced into the flue gas at 160 °C the NO conversion over the 8%Mn-2%Ce/TiO₂-PILC catalyst decreased from 57% to 52% and NO conversion was almost restored to its original value as H₂O was discontinued. After 2 h of a steady reaction at 160 °C the reaction temperature increased to 200 °C and 3 vol% H₂O was added again. NO conversion remained at 91.5%, which is the NO conversion obtained for the 8%Mn-2%Ce/TiO₂-PILC catalyst in the absence of H₂O at 200 °C. The results indicate that the inhibition effect of H₂O is related to the SCR reaction temperature and the poisoning effect was reversible.

Figure 9 shows the synergistic effects of SO₂ and H₂O on the SCR activity of the catalysts at 200 °C. The results indicated that when 3 vol% H₂O and 0.01 vol% SO₂ were added to the reaction gas the activities of the catalysts decreased significantly in just a few hours. The NO conversion of the 8%Mn/TiO₂-PILC catalyst decreased from 75%

Fig. 9. Effect of H₂O and SO₂ on NO conversion over the 8% Mn/TiO₂-PILC and 8%Mn-yCe/TiO₂-PILC catalysts. Reaction conditions: [NO] = [NH₃] = 0.06 vol%, [O₂] = 3 vol%, N₂ balance, total flow rate 300 ml/min.

to 28% in 2 h. The NO conversion did not recover even when SO₂ was removed from the flue gas. This clearly indicates that SO₂ has irreversible poisoning effects on the activity of the 8%Mn/TiO₂-PILC catalyst under low temperature SCR conditions. The deactivation of Mn/TiO₂ in the presence of SO₂ was also observed by Jin et al. [45]. Depositions of (NH₄)₂SO₄ and NH₄HSO₄ have been found on a Mn/TiO₂ surface at low temperature, which has led to an irreversible decrease in NO conversion.

Deactivation by H₂O and SO₂ was also observed over the 8%Mn-yCe/TiO₂-PILC catalysts. The activities of the 8%Mn-yCe/TiO₂-PILC catalysts were relatively higher than that of the 8%Mn/TiO₂-PILC catalyst in presence of H₂O and SO₂. Compared with other catalysts, the 8%Mn-2%Ce/TiO₂-PILC catalyst deactivation rate was especially delayed. The addition of Ce, especially at a loading of 2%, suppresses the deactivation to a degree although the SO₂ resistances of the xMn-yCe/TiO₂-PILC catalysts are weak.

3 Conclusions

Cerium modified MnO_x/TiO₂-PILC catalysts were prepared and showed high activity for the low temperature SCR of NO with NH₃. We found that Ti-pillared clays are a promising support for the low temperature SCR and that an optimal content of added ceria exists. For the 8%Mn-2%Ce/TiO₂-PILC catalyst the incorporation of cerium resulted in a good dispersion of manganese oxides on the surface of the catalysts. The reduction properties of the manganese oxides improved by the introduction of cerium and the XPS results confirmed that the higher amount of chemisorbed oxygen present on the 8%Mn-2%Ce/TiO₂-PILC catalyst facilitated the low-temperature SCR of NO with NH₃. Furthermore, strong Lewis acid sites were created when a proper amount

of cerium was added. All the catalysts based on the TiO₂-PILC catalyst showed good resistance to H₂O while the presence of SO₂ and H₂O resulted in the deactivation of the catalysts. More work is required to improve the H₂O and SO₂ resistance of the xMn-yCe/TiO₂-PILC catalysts at low temperature.

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第七届国际绿色能源会议暨第一届 DNL 洁净能源会议通知

第七届国际绿色能源会议暨第一届 DNL 洁净能源会议定于 2012 年 5 月 28~30 日在中国科学院大连化学物理研究所召开。会议由国际绿色能源协会及洁净能源国家实验室(筹)主办,中国科学院大连化学物理研究所承办。

本届会议旨在为参会的专家学者提供一个高水平的学术交流平台,共同探讨绿色能源及相关技术在全球的发展以及绿色能源相关产业面临的新机遇,从而推动国际绿色能源的技术创新和能源的可持续发展。

会议已邀请到多位国内外能源领域的著名专家学者、世界 500 强企业高管以及对能源领域有突出贡献的各国人士参会,并进行主题报告演讲。同时,还将举办绿色能源开发与利用、传统能源技术更新、能源科技发展、能源安全、节能减排与低碳经济等多场技术专题讨论会。

会议组委会热忱欢迎从事能源领域科学研究与技术开发的专家、同行及在读研究生积极投稿并莅临本届盛会!

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三、会议重要日期

- 2011-12-31 第一轮通知(稿件征集)
- 2012-03-01 网站投稿结束
- 2012-03-15 第二轮通知(论文录用通知及安排)
- 2012-04-01 折扣注册费截止

四、联系方式

刘慧颖
电话: 0411-84379577
传真: 0411-84665057
电子邮箱: liuhy@dicp.ac.cn

李颖

电话: 15998406335
电子邮箱: liy10@dicp.ac.cn
通信地址: 大连市中国科学院大连化学物理研究所
邮编: 110623

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