The Deactivation Mechanism of the Mo-Ce/Zr-PILC Catalyst Induced by Pb for the Selective Catalytic Reduction of NO with NH₃

Chenxi Li¹, Jin Cheng¹, Qing Ye¹,*©, Fanwei Meng¹, Xinpeng Wang¹ and Hongxing Dai²,*

1 Key Laboratory of Beijing on Regional Air Pollution Control, Department of Environmental Science, School of Environmental and Chemical Engineering, Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, China; lcx@emails.bjut.edu.cn (C.L.); chengjin3708@163.com (J.C.); MengFanwei@emails.bjut.edu.cn (F.M.); 17121679@bjtu.edu.cn (X.W.)
2 Beijing Key Laboratory for Green Catalysis and Separation, Key Laboratory of Beijing on Regional Air Pollution Control, Key Laboratory of Advanced Functional Materials, Education Ministry of China, and Laboratory of Catalysis Chemistry and Nanoscience, Department of Environmental Chemical Engineering, School of Environmental and Chemical Engineering, Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, China
* Correspondence: yeqing@bjut.edu.cn (Q.Y.); hxdai@bjut.edu.cn (H.D.)

Abstract: As a heavy metal, Pb is one component in coal-fired flue gas and is widely considered to have a strong negative effect on catalyst activity in the selective catalytic reduction of NO by NH₃ (NH₃-SCR). In this paper, we investigated the deactivation mechanism of the Mo-Ce/Zr-PILC catalyst induced by Pb in detail. We found that NO conversion over the 3Mo4Ce/Zr-PILC catalyst decreased greatly after the addition of Pb. The more severe deactivation induced by Pb was attributed to low surface area, lower amounts of chemisorbed oxygen species and surface Ce³⁺, and lower redox ability and surface acidity (especially a low number of Brønsted acid sites). Furthermore, the addition of Pb inhibited the formation of highly active intermediate nitrate species generated on the surface of the catalyst, hence decreasing the NH₃-SCR activity.

Keywords: Pb poisoning; Mo-Ce/Zr-PILC catalyst; NH₃-SCR; surface acidity

1. Introduction

Nitrogen oxides (NOₓ) are not only harmful to human health but are also important precursors of secondary pollution (e.g., photochemical smog, fine particles, and acid deposition) [1–3]. NH₃-SCR is an efficient and economical technology that has recently been used in the elimination of NOₓ from the exhausts of stationary and mobile sources. In addition, the V₂O₅–WO₃ (MoO₃)/TiO₂ catalysts are the most widely used catalyst systems in stationary sources [4]. However, these systems still have some inevitable practical defects, such as low N₂ selectivity in the high-temperature range, high SO₂ to SO₃ conversion rates, and the strong biological toxicity of vanadium species [5]. Therefore, it is urgent and necessary to develop a new SCR catalyst with low toxicity and high activity. Among the possible substitutes, Ce-based oxides have attracted extensive attention due to their excellent oxygen storage/release ability and redox performance [6,7]. It is reported that Mo modification could significantly promote the adsorption and activation of NH₃ species, which is beneficial for improvement in NH₃-SCR activity [8]. Therefore, Mo-Ce mixed-oxide catalysts have been extensively investigated. It was found that these materials were the most promising SCR catalysts [9], among which the Mo-Ce/Zr-PILC catalysts exhibited outstanding NH₃-SCR activity.

Deactivation induced by the poisoning of K, Na, Ca, Pb, or As is the main reason for the poor performance of the SCR catalysts. A number of experiments have been focused on the poisoning effects of alkali or alkaline earth metals on the NH₃-SCR catalyst [10,11].
However, very few studies have been done regarding the effects of heavy metals on the activity of SCR catalysts. Pb is a typical heavy metal contained in the flue gas derived from coal-fired and municipal solid waste incineration power plants. Tokarz et al. [12] observed a strong accumulation effect of Pb on the NH\textsubscript{3}-SCR catalyst, where the Pb concentration reached 3350 ppm after 1908 h operation of a municipal waste incinerator. This finding revealed that lead dust exhibited a strong accumulative poisoning effect on the NH\textsubscript{3}-SCR catalyst. However, there have been few reports in the literature on the poisoning mechanisms of heavy metals (e.g., Pb) on NH\textsubscript{3}-SCR catalysts. Hence, it is necessary to investigate the effects of Pb compounds on the performance of NH\textsubscript{3}-SCR catalysts and the involved deactivation mechanisms.

To elucidate the inhibitory effect of Pb on Mo-Ce/Zr-PILC in the NH\textsubscript{3}-SCR reaction, we prepared 3Mo4Ce/Zr-PILC (Mo and Ce contents were 3 and 4 wt%, respectively) and Pb-doped 3Mo4Ce/Zr-PILC catalysts. The physicochemical properties of these samples were characterized using the BET, XRD, H\textsubscript{2}-TPR, XPS, NH\textsubscript{3}-TPD, and in situ DRIFTS techniques. The main purpose of the present work is to clarify the effect of Pb doping on the catalytic performance of Ce-based catalysts, and to elucidate the involved poisoning mechanisms.

2. Experimental

2.1. Catalyst Preparation

The zirconium pillared clay was prepared using the pillaring method. An appropriate amount of zirconium oxychloride solution was added dropwise to the montmorillonite suspension, stirred for 12 h, aged at ambient room conditions for 24 h, dried at 100 °C for 12 h, and calcined at 400 °C for 2 h (named as Zr-PILC). The 3Mo/Zr-PILC catalyst with a Mo loading of 3 wt% was prepared by impregnating Zr-PILC with a proper amount of ammonium molybdate under stirring for 1 h, and then was put into a rotary evaporator to dry and calcine in air at 400 °C for 2 h. The 3Mo4Ce/Zr-PILC (Ce content was 4 wt%) catalyst was prepared by impregnating the 3Mo/Zr-PILC powders with a Ce(NO\textsubscript{3})\textsubscript{3} aqueous solution, and its preparation method followed the steps above. The catalysts poisoned by Pb were prepared using the impregnating method, by mixing the 3Mo4Ce/Zr-PILC catalyst with Pb(CH\textsubscript{3}COO)\textsubscript{2}·3H\textsubscript{2}O at different molar Pb/Ce ratios, and the subsequent procedures were the same as the steps above.

2.2. Catalyst Characterization

The crystal structures of the catalysts were determined using a Bruker D8 advance diffractometer (Bruker, Karlsruhe, Germany) equipped with a Cu Ka detector. N\textsubscript{2} adsorption–desorption isotherms were measured at −196 °C on a W-BK132F apparatus (JWGB, Beijing, China). X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher, Waltham, MA, USA) with Al Ka radiation (1486.6 eV) was used to analyze the surface compositions, metal oxidation states, and oxygen species of the catalysts. The sample powders were vacuumed, heated, and glued to the tape, and then the test was carried out immediately. The hydrogen temperature-programmed reduction (H\textsubscript{2}-TPR) and ammonia temperature-programmed desorption (NH\textsubscript{3}-TPD) experiments were carried out in a quartz U-tube reactor on a PCA-1200 analyzer (Beijing Builder Electronic Technology, Beijing, China) equipped with a thermal conductivity detector (TCD). Before H\textsubscript{2}-TPR measurement, the catalyst was pretreated in 5 vol% O\textsubscript{2}/N\textsubscript{2} flow at 400 °C for 1 h and then cooled to room temperature (RT). The H\textsubscript{2}-TPR profiles were recorded in a 5 vol% H\textsubscript{2}/N\textsubscript{2} flow of 30 mL/min from RT to 950 °C at a heating rate of 10 °C/min. Prior to NH\textsubscript{3}-TPD measurement, the catalyst was pretreated in a He flow of 30 mL/min at 400 °C for 1 h, followed by NH\textsubscript{3} adsorption at 100 °C. Subsequently, the catalyst was purged in a He flow of 30 mL/min for 30 min to remove the physically adsorbed NH\textsubscript{3}. Finally, the NH\textsubscript{3}-TPD profiles were recorded in a He flow of 30 mL/min from 30 to 850 °C at a heating rate of 10 °C/min. The in situ diffuse reflectance Fourier transform infrared spectroscopy (in situ DRIFTS) experiments were performed on a Bruker TENSOR II spectrometer (Bruker, Karlsruhe,
Germany). The catalyst was pretreated at 400 °C for 1 h to remove any adsorbed moisture and impurities. The background spectra were recorded by exposing the catalysts to a N₂ flow of 100 mL/min at 200 °C. The absorption spectra of NH₃ and (NO + O₂) were recorded in a 100 mL/min flow of (1100 ppm NH₃ + 1000 ppm NO + 4 vol% O₂ + 5 vol% H₂O + N₂ (balance)) and (1000 ppm NO + 4 vol% O₂ + N₂ (balance)), respectively.

2.3. NH₃-SCR Activity Evaluation

The activity measurements were performed in a fixed-bed quartz reactor using 0.3 g of the catalyst (40–60 mesh) mixed with 0.3 g of quartz sand (40–60 mesh). The simulated exhaust gas was composed of 1100 ppm NH₃ + 1000 ppm NO + 4 vol% O₂ + 5 vol% H₂O + N₂ (balance). The total flow rate of the feed gas was 500 mL/min, and the space velocity (SV) was 100,000 mL/(g h). NO concentrations were measured using a MODEL1080 analyser (Beijing SDL Technology, Beijing, China). The NO conversion was calculated according to the following equation:

\[
\text{NO conversion(\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\%
\]

3. Results and Discussion

3.1. NH₃-SCR Activity

In the present study, we investigated the poisoning effects that Pb had on the catalytic performance of 3Mo₄Ce/Zr-PILC. Figure 1 shows the NO conversion as a function of temperature (150–450 °C) over the 3Mo₄Ce/Zr-PILC and Pb-poisoned 3Mo₄Ce/Zr-PILC catalysts. Obviously, 3Mo₄Ce/Zr-PILC exhibited excellent catalytic activity, with a NO conversion of 90% in the 300–450 °C range. However, with a rise in the doped Pb amount of 3Mo₄Ce/Zr-PILC, NO conversion decreased considerably. When the Pb/Ce molar ratio was 0.2, catalytic efficiency in the whole temperature range was decreased by 5–25%. When the Pb/Ce molar ratio rose to 1, the activity of the catalyst was less than 50% at 150–450 °C. Obviously, the deNOₓ performance of the catalyst was greatly inhibited after Pb doping, and this inhibitive effect was enhanced with increasing Pb/Ce molar ratio.

![Figure 1. Catalytic activity for the NH₃-SCR reaction over the 3Mo₄Ce/Zr-PILC and Pb-poisoned 3Mo₄Ce/Zr-PILC catalysts under the reaction conditions of (1000 ppm NO + 1100 ppm NH₃ + 4 vol% O₂ + 5 vol% H₂O + N₂ (balance)) and SV = 100,000 mL/(g h).](image-url)
3.2. Crystal Phase and Textural Characteristics

The crystal phase compositions of the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts were measured using XRD. Figure 2 shows their diffraction patterns. According to our previous research [13], the XRD pattern of the PILC sample displayed a high-intensity basement (001) reflection peak at $2\theta = 9.3^\circ$, indicating that the montmorillonite clay possessed a regular and ordered interlayer structure. The (001) reflection peak of the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts was shifted to a lower angle and its intensity decreased, indicating an increase in interlayer distance and a disorder in the structure of the clay, which was caused by the effect of the strong delamination when the metal oxide entered the interlayer of clay. For the 3Mo4Ce/Zr-PILC catalyst, two-dimensional $hk$ reflections were present at $2\theta = 19.8^\circ$ and $34.9^\circ$, in which the former was a summation of the $hk$ indices of (02) and (11), while the latter was a summation of the $hk$ indices of (13) and (20) [14]. The peaks at $2\theta = 26.6^\circ$ and $28^\circ$ were reflections of the quartz and cristobalite impurities in the clay [15]. No diffraction peaks assignable to the crystalline cubic CeO$_2$ and MoO$_3$ were detected, suggesting that the cerium and molybdenum species were widely dispersed on the Zr-PILC surface, or were present in an amorphous state. As shown in Figure 2, after Pb doping, some obvious diffraction signals assignable to the PbMoO$_4$ phase were recorded at $2\theta = 27.5^\circ$, $29.5^\circ$, $32.9^\circ$, $37.8^\circ$, $44.9^\circ$, $47.3^\circ$, $50.9^\circ$, $55.7^\circ$, and $56.7^\circ$, and the intensity of the diffraction peaks ascribable to the PbMoO$_4$ phase increased gradually with a rise in Pb doping, indicating partial accumulation of the PbMoO$_4$ phase. The accumulation of the PbMoO$_4$ species would result in the partial deactivation of the 3Mo4Ce/Zr-PILC catalyst, which was consistent with its NH$_3$-SCR activity.

![Figure 2](image_url)

Figure 2. XRD patterns of the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts.

N$_2$ adsorption–desorption isotherms of the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts are shown in Figure 3. It can be seen that the isotherms of the catalysts were obviously in accordance with type I in the low relative pressure range, according to the IUPAC classification, which conformed to the characteristics of microporous materials [16]. The adsorbed volumes of the catalysts increased significantly in the $p/p_0$ (<0.01) range, which was due to the formation of a large number of micropores during the pillaring process. Additionally, the hysteresis loops of all of the catalysts corresponded to type H3, which appeared in the higher relative pressure range, indicating the presence of mesopores.

The textural parameters of the 3Mo4Ce/Zr-PILC and Pb-poisoned catalysts are listed in Table 1. As seen in Table 1, 3Mo4Ce/Zr-PILC displayed a surface area and a pore volume of 270 m$^2$/g and 0.164 cm$^3$/g, respectively. Additionally, it was noticeable that the doping of Pb resulted in significant decreases in surface area and pore volume, which might be
attributable to the partial blocking of the micropores in the catalysts, the agglomeration of the particles, or both.

![Graph showing N₂ adsorption-desorption isotherms](image)

**Figure 3.** N₂ adsorption-desorption isotherms of the 3Mo₄Ce/Zr-PILC and Pb-poisoned 3Mo₄Ce/Zr-PILC catalysts.

The SEM images of the 3Mo₄Ce/Zr-PILC and Pb-poisoned 3Mo₄Ce/Zr-PILC catalysts are shown in Figure 4. It can be observed that the 3Mo₄Ce/Zr-PILC catalyst displayed a microporous structure, while particles appeared on the surface of the Pb-poisoned catalysts. Moreover, for the Pb-poisoned 3Mo₄Ce/Zr-PILC catalysts with higher quantities of doped Pb, the number of particles increased but the pore size decreased, which was consistent with the BET results.

![SEM images](image)

**Figure 4.** SEM images of (A) 3Mo₄Ce/Zr-PILC, (B) 0.2Pb-Mo₄Ce/Zr-PILC, (C) 0.5Pb-Mo₄Ce/Zr-PILC, and (D) 1Pb-Mo₄Ce/Zr-PILC.
Table 1. BET surface areas and pore volumes of the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts.

| Catalyst            | BET Surface Area (m²/g) | Pore Volume (cm³/g) |
|---------------------|-------------------------|---------------------|
| 3Mo4Ce/Zr-PILC      | 270                     | 0.164               |
| 0.2Pb               | 259                     | 0.161               |
| 0.5Pb               | 256                     | 0.154               |
| 1Pb                 | 243                     | 0.152               |

3.3. Redox Properties

The redox property of a catalyst is an important factor in NH₃-SCR reactions. The reducibility of Ce and Mo species in Pb-free and Pb-doped catalysts was investigated using the H₂-TPR technique, so that the effect of Pb doping on the catalytic activity of 3Mo4Ce/Zr-PILC could be clarified. Meanwhile, after quantitative analysis of the H₂-TPR peaks, the H₂ consumption and reduction peak positions are summarized in Table 2. H₂-TPR profile of 3Mo4Ce/Zr-PILC displayed three main reduction peaks at 463, 527, and 723 °C (Figure 5), which could be interpreted as the reduction of the surface Ce⁴⁺ to Ce³⁺ species, co-reduction of the octahedrally structured well-dispersed Mo and iron species, and the co-reduction of the tetrahedrally structured Mo species and bulk CeO₂ species [17–19], respectively. In profiles of the Pb-poisoned catalysts, the first peak due to the reduction of the Ce species was shifted to a higher temperature, indicating that doping of Pb stabilized the Ce species and made it less reducible. The temperature of the low-temperature reduction peak increased in the order 3Mo4Ce/Zr-PILC (463 °C) > 0.2Pb-3Mo4Ce/Zr-PILC (470 °C) > 0.5Pb-3Mo4Ce/Zr-PILC (478 °C) > 1Pb-3Mo4Ce/Zr-PILC (483 °C), which was in accordance with their changing trend in SCR performance. In addition, two new reduction peaks at 575 and 790 °C appeared in the Pb-poisoned catalysts, which might be attributable to the reduction of the surface or bulk oxygen coordinated with the Pb atoms [20,21].

Figure 5. H₂-TPR profiles of the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts.
Table 2. Reduction peak temperatures and H$_2$ consumption of the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts.

| Catalyst          | Reduction Peak Temperature (°C) | H$_2$ Consumption (mmol/g) |
|-------------------|---------------------------------|----------------------------|
|                   | Peak 1  | Peak 2  | Peak 3  | Peak 4  | Peak 5  |
| 3Mo4Ce/Zr-PILC    | 463     | 527     | -      | 723     | -      | 0.79   |
| 0.2Pb             | 470     | 534     | 575    | 701     | 783    | 0.90   |
| 0.5Pb             | 478     | 531     | 580    | 711     | 776    | 1.01   |
| 1Pb               | 483     | 522     | 579    | 724     | 794    | 1.10   |

3.4. Surface Property

To gain better insights into the surface compositions and chemical states of the catalysts, we conducted XPS characterization, and the results are shown in Figure 6 and Table 3.

![Figure 6](image-url)

**Figure 6.** (A) Ce 3d and (B) O 1s spectra of the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts.

![Table 3](table-url)

Table 3. Surface element compositions of the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts.

| Catalyst          | Composition of Cerium Species (at%) | Composition of Oxygen Species (mol%) | Ce$^{3+}$/Ce$^{4+}$ Atomic Ratio |
|-------------------|------------------------------------|-------------------------------------|-------------------------------|
|                   | Ce$^{3+}$  | Ce$^{4+}$  | Ce$^{3+}$/Ce$^{4+}$ | O$^\alpha$  | O$^\beta$  | O$^\gamma$  |
| 3Mo4Ce/Zr-PILC    | 30.3      | 69.7       | 0.43              | 13.4        | 39.4        | 47.2        |
| 0.2Pb             | 26.2      | 73.8       | 0.36              | 13.1        | 34.7        | 52.2        |
| 0.5Pb             | 24.3      | 75.7       | 0.32              | 13.1        | 31.4        | 55.5        |
| 1Pb               | 21.1      | 78.9       | 0.27              | 13.4        | 24.8        | 61.8        |
Table 3. Surface element compositions of the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts.

| Catalyst          | Composition of Cerium Species (at%) | Composition of Oxygen Species (mol%) |
|-------------------|-------------------------------------|--------------------------------------|
|                   | Ce<sup>3+</sup> | Ce<sup>4+</sup> | Ce<sup>3+</sup>/Ce<sup>4+</sup> Atomic Ratio | O<sub>α</sub> | O<sub>β</sub> | O<sub>γ</sub> |
| 3Mo4Ce/Zr-PILC    | 30.3          | 69.7          | 0.43         | 13.4 | 39.4 | 47.2 |
| 0.2 Pb            | 26.2          | 73.8          | 0.36         | 13.1 | 34.7 | 52.2 |
| 0.5 Pb            | 24.3          | 75.7          | 0.32         | 13.1 | 31.4 | 55.5 |
| 1 Pb              | 21.1          | 78.9          | 0.27         | 13.4 | 24.8 | 61.8 |

The Ce 3d XPS spectra of the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts are presented in Figure 6A. The peaks labeled as v and u corresponded to Ce 3d<sub>5/2</sub> and Ce 3d<sub>3/2</sub> spin-orbit peaks [22,23], respectively, which could be deconvoluted into eight components: the u<sup>'</sup> and v<sup>'</sup> components were assigned to the surface Ce<sup>3+</sup> species corresponding to the 3d<sup>10</sup>4f<sup>1</sup> initial electronic state, while the other components were due to the surface Ce<sup>4+</sup> species corresponding to the 3d<sup>10</sup>4f<sup>0</sup> initial electronic state. The Ce<sup>3+</sup>/Ce<sup>4+</sup> atomic ratios were calculated according to the integral areas of the corresponding peaks. With an increase in Pb doping, the Ce<sup>3+</sup>/Ce<sup>4+</sup> atomic ratio decreased in the order 3Mo4Ce/Zr-PILC (0.43) > 0.2Pb-3Mo4Ce/Zr-PILC (0.36) > 0.5Pb-3Mo4Ce/Zr-PILC (0.32) > 1Pb-3Mo4Ce/Zr-PILC (0.27), which was the same trend seen in the catalytic activity. The Ce<sup>3+</sup> species exerted a positive effect on catalytic activity owing to its strong ability to create charge imbalance and form oxygen vacancies and unsaturated chemical bonds on the catalyst surface, which could increase the amount of surface chemisorbed oxygen species [24]. Some oxygen vacancies were occupied due to Pb introduction, which inhibited the transformation of Ce<sup>4+</sup> to Ce<sup>3+</sup>. Therefore, the decrease in the amount of the surface Ce<sup>3+</sup> species on 1Pb-3Mo4Ce/Zr-PILC was an important parameter that gave rise to this system’s worse catalytic activity.

O 1s XPS spectra of the catalysts are illustrated in Figure 6B, which could be decomposed into three components at BE = 532.61–532.70, 531.48–531.78, and 530.16–531.36 eV, assignable to the surface lattice oxygen of the Si–O bond (O<sub>γ</sub>), chemisorbed oxygen (O<sub>β</sub>), and lattice oxygen (O<sub>α</sub>) [25–27], respectively. Chemisorbed oxygen was mainly the oxygen species adsorbed at the oxygen vacancies, as well as the defect oxides and hydroxyl-like groups. Based on that curve-fitting approach, the O<sub>β</sub> concentrations on the surface of the catalysts were calculated, and the results are listed in Table 3. A distinct decrease in the amount of O<sub>β</sub> species was observed after the Pb doping. The O<sub>β</sub>/(O<sub>α</sub> + O<sub>β</sub> + O<sub>γ</sub>) molar ratio decreased in the order 3Mo4Ce/Zr-PILC (0.394) > 0.2Pb-3Mo4Ce/Zr-PILC (0.347) > 0.5Pb-3Mo4Ce/Zr-PILC (0.314) > 1Pb-3Mo4Ce/Zr-PILC (0.248). These results were consistent with the order of NH<sub>3</sub>-SCR activity, indicating that the lower amounts of O<sub>β</sub> species on the Pb-poisoned catalysts were also responsible for their lower catalytic activities. It has been previously demonstrated that O<sub>β</sub> species are the most effective oxygen species in the SCR reaction [27]. Moreover, the oxygen in the gas phase and the oxygen adsorbed on the catalyst surface could be easily exchanged with the O<sub>β</sub> species, and the active transportation of the O<sub>β</sub> species could also facilitate the SCR reaction [28].

3.5. Surface Acidity

The NH<sub>3</sub> adsorption capacity has been widely reported to influence the SCR reaction, and it has also been strongly associated with the surface acidity of a catalyst [29]. Therefore, NH<sub>3</sub>-TPD experiments on the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts were carried out to examine the influence of Pb doping on surface acidity, and the results are illustrated in Figure 7.
Table 4. NH₃-TPD temperatures and desorption amounts of the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts.

| Catalyst                | Temperature (°C) | Acidity (mmol\textsubscript{NH₃}/g) | Total Desorption Amount (mmol\textsubscript{NH₃}/g) |
|------------------------|------------------|-------------------------------------|-----------------------------------------------|
|                        | Weak Peak | Medium Peak | Strong Peak | Weak Peak | Medium Peak | Strong Peak |                                                              |
| 3Mo4Ce/Zr-PILC         | 171      | 220        | 311        | 0.046    | 0.131      | 0.087      | 0.264                                                      |
| 0.2Pb                  | 166      | 215        | 305        | 0.043    | 0.125      | 0.079      | 0.247                                                      |
| 0.5Pb                  | 173      | 223        | 310        | 0.040    | 0.103      | 0.070      | 0.213                                                      |
| 1Pb                    | 163      | 214        | 301        | 0.042    | 0.096      | 0.064      | 0.202                                                      |

Figure 7. NH₃-TPD profiles of the 3Mo4Ce/Zr-PILC and Pb-poisoned 3Mo4Ce/Zr-PILC catalysts.

There were three desorption peaks in the NH₃-TPD profile of each sample (Figure 7). The first peak was located at 163–173 °C, and signified the desorption of the physically adsorbed NH₃ species and some NH₄⁺ species at the weak Brønsted acid sites (i.e., weak acid sites); the second peak at 214–223 °C was attributed to the NH₄⁺ species desorbed from the strong Brønsted acid sites (i.e., medium acid sites); and the third peak at 301–311 °C was assigned to the desorption of the coordinated NH₃ bound to the Lewis acid sites (i.e., strong acid sites) [29,30]. Acid site numbers were quantitatively analyzed according to the NH₃-TPD profiles, as listed in Table 4. The amount of Brønsted acid sites was in the order: 3Mo4Ce/Zr-PILC (0.131 mmol/g) > 0.2Pb-3Mo4Ce/Zr-PILC (0.125 mmol/g) > 0.5Pb-3Mo4Ce/Zr-PILC (0.103 mmol/g) > 1Pb-3Mo4Ce/Zr-PILC (0.096 mmol/g). The total acid amount decreased in the sequence 3Mo4Ce/Zr-PILC (0.202 mmol/g) > 0.2Pb-3Mo4Ce/Zr-PILC (0.247 mmol/g) > 0.5Pb-3Mo4Ce/Zr-PILC (0.213 mmol/g) > 1Pb-3Mo4Ce/Zr-PILC (0.202 mmol/g). It is noteworthy that a substantial decrease in the desorbed ammonia amount was observed when the amount of doped Pb increased. One reason for this phenomenon was probably due to the agglomeration of Pb species on the catalyst surface, partially blocking the micropores and covering some of the acid sites in the catalyst. In addition, it can be seen from the above Ce 3d XPS results that the concentration of the surface Ce³⁺ species on the sample decreased after Pb doping. According to the literature [31], the decrease in Ce³⁺ atomic concentration leads to a decrease in amount of oxide defects or hydroxyl-like groups, resulting in a decrease in the number of Brønsted acid sites. Therefore, we can conclude that the reduced number of acid sites (especially Brønsted acid sites) in the Pb-poisoned catalysts was one of the main reasons for the decrease in catalytic activity.
3.6. Switching Feed Gas from NO + O2 + N2 + NH3 to NO + O2 + N2 on Various Catalysts

In order to investigate activity of the NOx species and their role in the NH3-SCR reaction, transient experiments were performed over the 3Mo4Ce/Zr-PILC catalyst. Figure 8 shows the DRIFTS spectra at 200 °C recorded after switching from 1100 ppm NH3 + 1000 ppm NO + 4% O2 + N2 (balance) to a flow containing 1000 ppm NO + 4% O2 + N2 (balance) over the 3Mo4Ce/Zr-PILC catalyst.

![Figure 8](image)

**Figure 8.** In situ DRIFTS spectra of the 3Mo4Ce/Zr-PILC catalyst exposed to (1100 ppm NH3 + 1000 ppm NO + 4% O2 + N2 (balance)) for 1 h and then switched to (1000 ppm NO + 4% O2 + N2 (balance)) for 1 h at 200 °C.

From the transient experimental results of the 3Mo4Ce/Zr-PILC catalyst, it can be seen that bands attributable to the nitrate species and NH3 species appeared on the surface of 3Mo4Ce/Zr-PILC after the flow containing NH3 + NO + O2 + N2 was introduced. Several bands were observed at 1430, 1600, 1680, and 3200–3400 cm\(^{-1}\), in which the bands at 1430 and 1680 cm\(^{-1}\) were attributed to the symmetric bending vibrations of NH4\(^+\) that was chemisorbed at the Brønsted acid sites, and the band at 3200–3400 cm\(^{-1}\) was assigned to the NH3 species adsorbed at the Lewis acid sites [32]. In addition, the band at 1600 cm\(^{-1}\) could be ascribed to the bridged nitrate, and the band attributable to the adsorbed nitrogen oxide species was at 1680 cm\(^{-1}\) [31,33]. It is well known that the adsorbed NOx species can participate in the “fast NH3-SCR” reaction, which promotes the NH3-SCR performance [34]. When the feed gas was switched to NO + O2 + N2, the bands at 1430 and 3200–3400 cm\(^{-1}\) disappeared rapidly with respect to time, indicating that the NH3 adsorbed at the Lewis and Brønsted acid sites reacted with the nitrate species, and the NH3 species were gradually consumed during the reaction. Simultaneously, the intensity of the bands at 1331 and 1600 cm\(^{-1}\) was attributable to monodentate nitrate, and bridge nitrate also increased rapidly, indicating that the monodentate nitrates and bridge nitrites were highly active NOx species and played an important role in the NH3-SCR reaction.

Figure 9 shows the DRIFTS spectra of the 1Pb-3Mo4Ce/Zr-PILC catalyst. The band intensity of the NH3 species at 1430 and 3200–3400 cm\(^{-1}\) was lower than that of the 3Mo4Ce/Zr-PILC catalyst after exposure to a flow of NH3 + NO + O2 + N2. The intensity of the bands at 1365 and 1604 cm\(^{-1}\) was attributable to the monodentate nitrate, and bridge nitrate also increased slightly after cutting off NH3 introduction. These results indicate that the doping of Pb inhibited the adsorption of the NH3 species on the 1Pb-3Mo4Ce/Zr-PILC catalyst, and less of the main active species monodentate nitrate and bridge nitrate were generated, which would influence NH3-SCR activity of the catalyst.
Figure 9. In situ DRIFTS spectra of the 1Pb-3Mo4Ce/Zr-PILC catalyst exposed to (1100 ppm NH$_3$ + 1000 ppm NO + 4% O$_2$ + N$_2$ (balance)) for 1 h and then switched to (1000 ppm NO + 4% O$_2$ + N$_2$ (balance)) for 1 h at 200 °C.

Therefore, it can be concluded that the monodentate nitrate, bridge nitrate, and adsorbed NO$_2$ species were the highly active intermediate species which could promote the NH$_3$-SCR reaction. Meanwhile, the doping of Pb inhibited the formation of intermediate nitrate species on the surface of the catalyst, thereby inhibiting the NH$_3$-SCR activity.

3.7. Pb Poisoning Mechanism

Pb is an ingredient found in coal-fired flue gas and inhibits SCR catalysts. The DeNO$_x$ performance of the catalyst was greatly suppressed after the Pb doping, and this inhibition effect was enhanced with increasing Pb/Ce molar ratio. XRD patterns (Figure 2) and SEM images (Figure 4) demonstrate that there was obvious agglomeration of the metal oxides after the Pb doping, and some PbMoO$_4$ species were generated on the surface of the catalysts. In combination with the Ce 3d XPS results (Figure 6A), this suggests that Pb might occupy the oxygen vacancies in ceria, which could weaken the Ce$^{3+}$ ↔ Ce$^{4+}$ redox cycle and suppress the surface Ce$^{4+}$ → Ce$^{3+}$ transformation. In addition, based on the characterization results of NH$_3$-TPD (Figure 7), the number of both Bronsted and Lewis acid sites decreased significantly (especially the number of Bronsted acid sites) after the Pb doping. Since NH$_3$ was more readily adsorbed on the catalyst surface than NO in the SCR reaction, the adsorbed ammonia species were critical in the SCR reaction [35]. Furthermore, Pb inhibited the formation of the intermediate nitrate species (i.e., monodentate nitrates and bridge nitrates) on the surface of catalysts in the SCR reaction. The decrease in ammonia absorbance at the acid sites, the decrease of the highly active intermediate species, and the vanishing of active ammonia species were the most important influencing factors in the Pb-induced deactivation of the 3Mo4Ce/Zr-PILC catalyst.

4. Conclusions

Pb doping caused a serious deactivation of the 3Mo4Ce/Zr-PILC catalyst for the NH$_3$-SCR reaction in this study. NO conversion decreased from 98% to 49% over the 3Mo4Ce/Zr-PILC catalyst at 450 °C when the Pb/Ce molar ratio was 1. The characterization results revealed that as the amount of surface Ce$^{3+}$ and chemisorbed oxygen species increased, the interaction between PbO and 3Mo4Ce/Zr-PILC increased as well, with more PbMoO$_4$ species formed on the catalyst surface, less intermediate nitrate species, and lower redox ability and surface acidity.
Author Contributions: Conceptualization, C.L. and J.C.; Methodology, C.L. and J.C.; Formal analysis, C.L.; Investigation, C.L. and J.C.; Software, F.M. and X.W.; Validation, Q.Y.; Writing—original draft, C.L. and J.C.; Writing—review& editing, C.L., Q.Y. and H.D.; Supervision, Q.Y. and H.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: This work was supported by the National Natural Science Foundation of China (Grant Nos. 21277008 and 20777005) and the National Key Research and Development Program of China (Grant No. 2017YFC0209905).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Shan, W.; Yu, Y.; Zhang, Y.; He, G.; Peng, Y.; Li, J.; He, H. Theory and practice of metal oxide catalyst design for the selective catalytic reduction of NO with NH3. Catal. Today 2021, 376, 292–301. [CrossRef]
2. Zhang, X.; Diao, Q.; Hu, X.; Wu, X.; Xiao, K.; Wang, J. Modification of V2O5-WO3/TiO2 catalyst by loading of MnO2 for enhanced low-temperature NH3-SCR performance. Nanomaterials 2020, 10, 1900. [CrossRef] [PubMed]
3. Xu, W.; Zhang, G.; Chen, H.; Zhang, G.; Han, Y.; Chang, Y.; Gong, P. Mn/β and Mn/ZSM-5 for the low-temperature selective catalytic reduction of NO with ammonia: Effect of manganese precursors. Chin. J. Catal. 2018, 39, 118–127. [CrossRef]
4. Zhang, N.; He, H.; Wang, D.; Li, Y. Challenges and opportunities for manganese oxides in low-temperature selective catalytic reduction of NO3 with NH3:H2O resistance ability. J. Solid State Chem. 2020, 289. [CrossRef]
5. Chen, L.; Li, J.; Ge, M. Promotional effect of Ce-doped V2O5-WO3/TiO2 with low vanadium loadings for selective catalytic reduction of NO by NH3. J. Phys. Chem. C 2009, 113, 21177–21184. [CrossRef]
6. Hao, Z.; Jiao, Y.; Shi, Q.; Zhang, H.; Zhan, S. Improvement of NH3-SCR performance and SO2 resistance over Sn modified CeMoO4 electrospun fibers at low temperature. Catal. Today 2019, 327, 37–46. [CrossRef]
7. Xiong, Y.; Tang, C.; Yao, X.; Zhang, L.; Li, L.; Wang, X.; Deng, Y.; Gao, F.; Dong, L. Effect of metal ions doping (M = Ti4+, Sn4+) on the catalytic performance of MnOx/Co catalyst for low temperature selective catalytic reduction of NO with NH3. Appl. Catal. A Gen. 2015, 495, 206–216. [CrossRef]
8. Zhan, S.; Shi, Q.; Zhang, Y.; Li, Y.; Tian, Y. Preparation of novel CeMo3 hollow microspheres for low-temperature SCR removal of NOx with NH3. RSC Adv. 2016, 6, 59185–59194. [CrossRef]
9. Tang, X.; Shi, Y.; Gao, F.; Zhao, S.; Yi, H.; Xie, Z. Promotional role of Mo on Ce0.3FeOx catalyst towards enhanced NH3-SCR catalytic performance and SO2 resistance. Chem. Eng. J. 2020, 398. [CrossRef]
10. Li, L.; Chen, L.; Kong, M.; Liu, Q.; Ren, S. New insights into the deactivation mechanism of V2O5-WO3/TiO2 catalyst during selective catalytic reduction of NO with NH3: Synergies between arsenic and potassium species. RSC Adv. 2019, 9, 37724–37732. [CrossRef]
11. Wang, H.; Chen, X.; Gao, S.; Wu, Z.; Liu, Y.; Weng, X. Deactivation mechanism of Ce/TiO2 selective catalytic reduction catalysts by the loading of sodium and calcium salts. Catal. Sci. Technol. 2013, 3, 715–722. [CrossRef]
12. Tokarz, M.; Jarars, S.; Persson, B. Poisoning of De-NOx SCR catalyst by flue gases from a waste incineration plant. In Catalysis Deactivation 1991; Proceedings of the 5th International Symposium, Studies in Surface Science & Catalysis; Elsevier: Amsterdam, The Netherlands, 1991; Volume 68, pp. 523–530.
13. Cheng, J.; Ye, Q.; Li, C.; Cheng, S.; Kang, T.; Dai, H. Ceria-modified Al-Mn-pillared clay catalysts for the selective catalytic reduction of NO with NH3 at low temperatures. Asia Pac. J. Chem. Eng. 2019, 15.
14. Yang, S.; Fu, Y.; Liao, Y.; Xiong, S.; Qu, Z.; Yan, N.; Li, J. Competition of selective catalytic reduction and non-selective catalytic reduction over MnOx/TiO2 for NO removal: The relationship between gaseous NO concentration and N2O selectivity. Catal. Sci. Technol. 2014, 4, 224–232. [CrossRef]
15. Zang, S.; Zhang, G.; Qi, W.; Song, L.; Zhang, R.; He, H. Resistance to SO2 poisoning of V2O5/TiO2-PILC catalyst for the selective catalytic reduction of NO by NH3. Chin. J. Catal. 2016, 37, 888–897. [CrossRef]
16. Li, C.; Cheng, J.; Ye, Q.; Meng, F.; Wang, X.; Dai, H. Poisoning effects of alkali and alkaline earth metal doping on selective catalytic reduction of NO with NH3 over the Nb-Ce/Zr-PILC catalysts. Catalysts 2021, 11, 329. [CrossRef]
17. Gao, G.; Shi, J.; Liu, C.; Gao, C.; Fan, Z.; Niu, C. Mn/CeO2 catalysts for SCR of NOx with NH3: Comparative study on the effect of supports on low-temperature catalytic activity. Appl. Surf. Sci. 2017, 411, 338–346. [CrossRef]
18. Ding, S.; Liu, F.; Shi, X.; Liu, K.; Lian, Z.; Xie, L.; He, H. Significant promotion effect of Mo additive on a novel Ce-Zr mixed oxide catalyst for the selective catalytic reduction of NOx with NH3. ACS Appl. Mater. Interfaces 2015, 7, 9497–9506. [CrossRef]
19. Rajkumar, T.; Sapi, A.; Abel, M.; Kiss, J.; Szentl, I.; Baan, K.; Gomez-Perez, J.F.; Kukovecz, A.; Konya, Z. Surface engineering of CeO2 catalysts: Differences between solid solution based and interfacially designed Ce1-xMxO2 and MO/CeO2 (M = Zn, Mn) in CO2 hydrogenation reaction. Catal. Lett. 2021. [CrossRef]
20. Zhou, L.; Li, C.; Zhao, L.; Zeng, G.; Gao, L.; Wang, Y.; Yu, M. The poisoning effect of PbO on Mn-Ce/TiO$_2$ catalyst for selective catalytic reduction of NO with NH$_3$ at low temperature. *Appl. Surf. Sci.* 2016, 389, 532–539. [CrossRef]

21. Gao, X.; Du, X.; Fu, Y.; Mao, J.; Luo, Z.; Ni, M.; Cen, K. Theoretical and experimental study on the deactivation of V$_2$O$_5$ based catalyst by lead for selective catalytic reduction of nitric oxides. *Catal. Today* 2011, 175, 625–630. [CrossRef]

22. Wang, P.; Chen, S.; Gao, S.; Zhang, J.; Wang, H.; Wu, Z. Niobium oxide confined by ceria nanotubes as a novel SCR catalyst with excellent resistance to potassium, phosphorus, and lead. *Appl. Catal. B Environ.* 2018, 231, 299–309. [CrossRef]

23. Wang, J.; Dong, X.; Wang, Y.; Li, Y. Effect of the calcination temperature on the performance of a CeMoO$_x$ catalyst in the selective catalytic reduction of NO by ammonia. *Catal. Today* 2015, 245, 10–15. [CrossRef]

24. Liu, J.; Shi, X.; Shan, Y.; Yan, Z.; Shan, W.; Yu, Y.; He, H. Hydrothermal stability of CeO$_2$-WO$_3$-ZrO$_2$ mixed oxides for selective catalytic reduction of NO by NH$_3$. *Environ. Sci. Technol.* 2018, 52, 11769–11777. [PubMed]

25. Xu, H.; Wang, Y.; Cao, Y.; Fang, Z.; Lin, T.; Gong, M.; Chen, Y. Catalytic performance of acidic zirconium-based composite oxides monolith catalyst on selective catalytic reduction of NO with NH$_3$. *Chem. Eng. J.* 2014, 240, 62–73. [CrossRef]

26. Li, L.; Tan, W.; Wei, X.; Fan, Z.; Liu, A.; Guo, K.; Ma, K.; Yu, S.; Ge, C.; Tang, C.; et al. Mo doping as an effective strategy to boost low temperature NH$_3$-SCR performance of CeO$_2$/TiO$_2$ catalysts. *Catal. Commun.* 2016, 114, 10–14. [CrossRef]

27. Jiang, Y.; Yang, L.; Liang, G.; Liu, S.; Gao, W.; Yang, Z.; Lin, R.; Zhu, X. The poisoning effect of PbO on CeO$_2$-MoO$_3$/TiO$_2$ catalyst for selective catalytic reduction of NO with NH$_3$. *Mol. Catal.* 2020, 486. [CrossRef]

28. Yan, Z.; Shi, X.; Yu, Y.; He, H. Alkali resistance promotion of Ce-doped vanadium-titanic-based NH$_3$-SCR catalysts. *J. Environ. Sci.* 2018, 73, 155–161. [CrossRef] [PubMed]

29. Liu, Z.; Zhang, S.; Li, J.; Ma, L. Promoting effect of MoO$_3$ on the NO$_x$ reduction by NH$_3$ over CeO$_2$/TiO$_2$ catalyst studied with in situ DRIFTS. *Appl. Catal. B Environ.* 2014, 144, 90–95. [CrossRef]