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DRIFT Study on Promotion Effect of the Keggin Structure over V_2O_5 - MoO_3/TiO_2 Catalysts for Low Temperature NH_3 -SCR Reaction

Rui Wu ^{1,†}, Ningqiang Zhang ^{1,†}, Lingcong Li ¹, Hong He ^{1,2,*}, Liyun Song ^{1,*} and Wenge Qiu ¹

¹ Laboratory of Catalysis Chemistry and Nanoscience, Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China; wuruicoco@sina.com (R.W.); zhangningqiang08@163.com (N.Z.); lilingcong1988@163.com (L.L.); qiuwenge@bjut.edu.cn (W.Q.)

² Collaborative Innovation Center of Electric Vehicles in Beijing, Beijing 100081, China

* Correspondence: hehong@bjut.edu.cn (H.H.), songly@bjut.edu.cn (L.S.)

† These authors contributed equally.

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Abstract: Heteropoly acids (HPAs) with the Keggin structure have been widely used in NO_x removal. Two kinds of catalysts (those with and without the Keggin structure) are prepared for studying the effect of the Keggin structure on the NH_3 -SCR reaction. A series of in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) analyses are conducted to investigate the surface-adsorbed species on the catalysts during the SCR reaction. The mechanism for enhancing low-temperature activity of the catalysts is proposed. Furthermore, the effect of NH_4^+ in the Keggin structure is also investigated. Results indicate that both the Langmuir–Hinshelwood (L-H) and Eley–Rideal (E-R) mechanisms occurred in the NH_3 -SCR reaction over the catalyst with the Keggin structure (Cat-A); in addition, when more acid sites are provided, NO_x species activity is improved and more NH_4^+ ions participate in reaction over Cat-A, thus promoting SCR activity.

Keywords: NH_3 -SCR; in situ DRIFT; Keggin structure; surface adsorption

1. Introduction

NO_x is an air pollutant that can result in a variety of pollution, such as acid rain, optical chemical smog, and the greenhouse effect. NO_x is emitted when using fossil fuels in industrial facilities and automobiles [1,2]. Selective catalytic reduction (SCR) has been extensively used to remove NO_x emissions from stationary sources such as coal-fired boilers [3]. The commercialized catalyst used in SCR has mainly been V_2O_5 - WO_3/TiO_2 (or V_2O_5 - MoO_3/TiO_2), which has high activity and good SO_2 tolerance. However, it has a very narrow operating temperature (300–400 °C), high conversion of SO_2 to SO_3 , and low N_2 selectivity at high temperatures [4,5]. Therefore, developing an NH_3 -SCR catalyst with good catalytic performance at low temperature is desirable.

Heteropoly acids (HPAs) have unique structure and extraordinarily strong acidity, and, as such, HPAs have attracted the attention of many researchers [6,7]. The main kind of HPAs used in catalytic applications is Keggin HPAs, such as $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, and $H_3SiW_{12}O_{40}$ [8]. It has been found that NO can be effectively absorbed on 12-tungstophosphoric acid at 150 °C and decomposed at about 450 °C upon rapid heating. It has been reported that small polar molecules (such as NO , NH_3 , and H_2O) can access the secondary structure of Keggin HPAs and that SO_2 cannot influence adsorption of NO . Supplementary experiments showed that NO can replace the structural water present between Keggin units of HPAs [9,10]. Later, some researchers used aromatic hydrocarbons loaded with Pt and Pd to improve the activity of NO reduction [11,12]. Putluru et al. reported that HPAs can promote SCR

activity and shows excellent alkali deactivation resistance [13]. Weng et al. used 12-tungstaphosphoric acid loaded on CeO_2 and found that the catalyst had significantly improved performance in the SCR reaction and improved SO_2 poisoning resistance [14]. Ammonium salts are more available than HPAs, and using 12-tungstophosphoric acid ammonium salt for NO_x removal has been reported. Moffat et al. found an interesting phenomenon; specifically, that the ammonium salt of 12-tungstophosphoric acid exhibited better NO_x removal capacity in the case without NH_3 because bound NH_4^+ on the solid can react with absorbed NO_2 to produce N_2 , and ammonium salt can be regenerated from gaseous NH_3 [9]. However, there are few reports about using ammonium salts of HPAs for SCR, and further research on the effect of the Keggin structure and that of the NH_4^+ of ammonium salts on SCR is lacking.

In this research, $\text{V}_2\text{O}_5\text{-(NH}_4)_3\text{PMo}_{12}\text{O}_{40}/\text{TiO}_2$ and a conventional oxide catalyst are prepared for studying the effect of the Keggin structure on the NH_3 -SCR reaction. A series of in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) analyses are conducted to investigate surface-adsorbed species. Fourier Transform infrared spectroscopy (FT-IR) is used to evaluate the effect of NH_4^+ of ammonium salts on the catalysts.

2. Results and Discussion

2.1. Catalytic Activity

Catalytic performances of the catalysts with and without the Keggin structure at elevated temperature are shown in Figure 1. Structures of the two samples were determined using X-ray diffraction (XRD) and Raman spectroscopy (Figures S1 and S2, respectively). X-ray Fluorescence Spectrometer (XRF) results of elemental analysis and the BET specific surface area data are shown in Table S1. Results show that Cat-A, which has the Keggin structure, had the same composition and BET surface area as Cat-B, which has an oxide phase. As shown in Figure 1, Cat-A had much higher SCR activity than Cat-B. NO conversion over Cat-A reached 93% at 220 °C and showed no obvious decline until 350 °C. In contrast, NO conversion over Cat-B was only 67% at 220 °C. Clearly, the catalyst with the Keggin structure had improved NO conversion in low temperature. Both catalysts had excellent N_2 selectivity of 99% below 250 °C. The time-on-stream stability was investigated (Figure S5). The NO_x conversion over Cat-A decreased from 100% to 95% in 20 h, while, for Cat-B, it decreased from 99% to 92%. Therefore, Cat-A exhibited better time-on-stream stability than Cat-B.

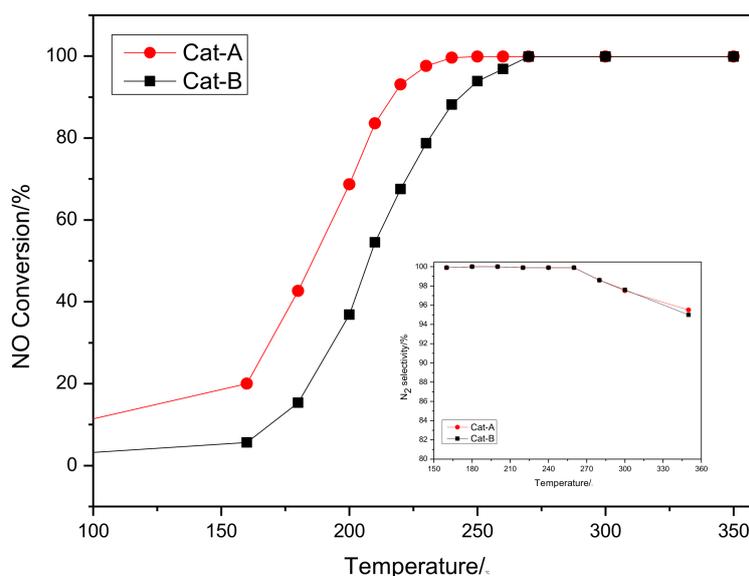


Figure 1. NO conversion of the two catalysts. (Reaction conditions: NO 1000 ppm, $\text{NH}_3/\text{NO} = 1$, O_2 5%, H_2O 5%, SO_2 350 ppm, N_2 balance, and $\text{GHSV} = 40,000 \text{ h}^{-1}$).

2.2. Adsorption Behaviors of Reactants on the Surface of the Catalysts (In Situ DRIFT)

2.2.1. NH₃ Adsorption on the Surface of the Catalysts

In situ DRIFT spectra of NH₃ adsorption on Cat-A and Cat-B at 250 °C are shown in Figure 2. As seen in Figure 2A, there were six bands: 1211, 1391, 1454, 1596, 1685, and 1737 cm⁻¹. The peaks centered at 1454 cm⁻¹ and in the range of 1750–1650 cm⁻¹ can be, respectively, attributed to asymmetric and symmetric bending (δ_{as} and δ_s) vibrations of NH₄⁺ species on Brönsted acid sites [15–17]. The bands at 1211 and 1391 cm⁻¹ can be assigned to N-H bonds in NH₃ that is chemisorbed on Lewis acid sites [18].

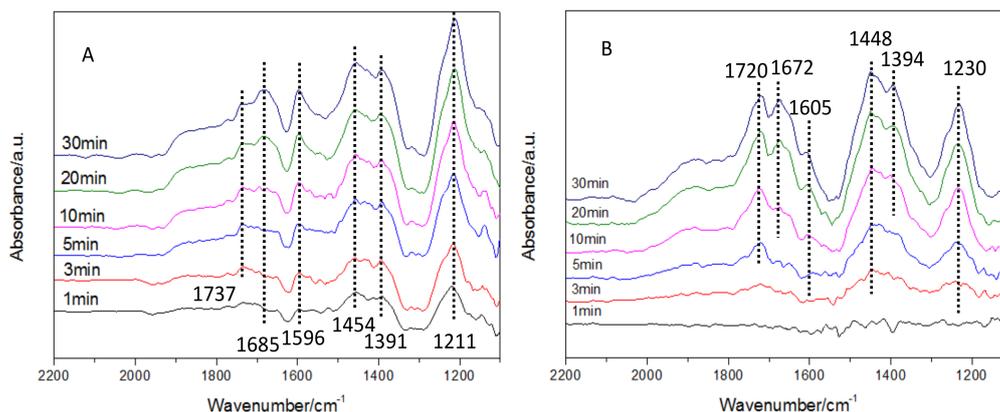


Figure 2. DRIFT spectra for NH₃ adsorption at 250 °C on: (A) Cat-A; and (B) Cat-B.

As illustrated in Figure 2B, DRIFT spectra for NH₃ adsorption over Cat-B were similar to those for NH₃ adsorption over Cat-A. A broad absorption band at 1448 cm⁻¹ was ascribed to δ_{as} NH₄⁺ vibration and the bands at 1750–1650 cm⁻¹ were due to δ_s NH₄⁺ vibration [19]. Coordinated δ_s NH₃ (1230 and 1394 cm⁻¹) and δ_{as} NH₃ species (1605 cm⁻¹) on Lewis acid sites were also observed [20,21]. It is evident that the intensity of the band assigned to Lewis acid sites (1230 cm⁻¹) is much weaker than that over Cat-A. It is known that HPAs have stronger (Brönsted) acidity, but it was reported that (NH₄)₃PMo₁₂O₄₀ provides Lewis acid sites that were strong at high temperature because of the oxygen-deficient Keggin structure [22]. The NH₃-desorption peaks in the temperature programmed desorption of ammonia (NH₃-TPD) was interconnected to the concentration of acid sites [23]. Combined with the results for NH₃-TPD (Figure S3), the peak area of Cat-A was more than Cat-B, which suggested that the concentration of Lewis acid sites was more than Cat-B. As reported, the high amount of Lewis acid site could improve the low temperature activity [24]. Therefore, the Keggin structure not only provides more Brönsted acid sites, but also offered Lewis acid sites that are beneficial for low-temperature SCR catalytic activity.

2.2.2. Co-Adsorption of NO + O₂ on the Surface of the Catalysts

Figure 3 shows DRIFT results of NO + O₂ co-adsorption on the surface of Cat-A and Cat-B. Adsorbed species on the two catalysts are clearly very different. As seen in Figure 3A, there are several distinct bands at 1347, 1513, 1640, 1668, 1786, 1751, 1860, and 1976 cm⁻¹. A broad band at 1347 cm⁻¹ appeared first and can be ascribed to free nitrate ions [25]. Later, smaller bands at 1513, 1640, and 1668 cm⁻¹ were observed, and these can be assigned to bidentate nitrate, adsorbed NO₂, and adsorbed N₂O₄, respectively [20,26]. Bands at 1751 and 1786 cm⁻¹ can be ascribed to adsorption of trans-(NO)₂ [25,27]. A weaker band at 1860 cm⁻¹ can be assigned to surface bound NO [28]. The band at 1976 cm⁻¹ increased with time and can be ascribed to NO in the secondary structure of Keggin anions [28]. For Cat-B (Figure 3B), a series of peaks can be ascribed to monodentate nitrates (1317 and 1490 cm⁻¹), free nitrate ions (1340 cm⁻¹), and adsorbed NO₂ (1647 cm⁻¹) [29,30]. For Cat-B, there

were fewer kinds of adsorbed NO_x species than for Cat-A. Over Cat-B, there were more monodentate nitrates than free nitrate ions. It is reported that, for NSR, NO_x was primarily trapped by the metal ions (such as K or Li) in free nitrate ions, thus leading to increased trapping capacity of NO_x [31,32]. It is likely that NH_4^+ in Cat-A plays the same role in trapping NO_x , and this indicates that the NO_x storage behavior of Cat-A is better than that of Cat-B.

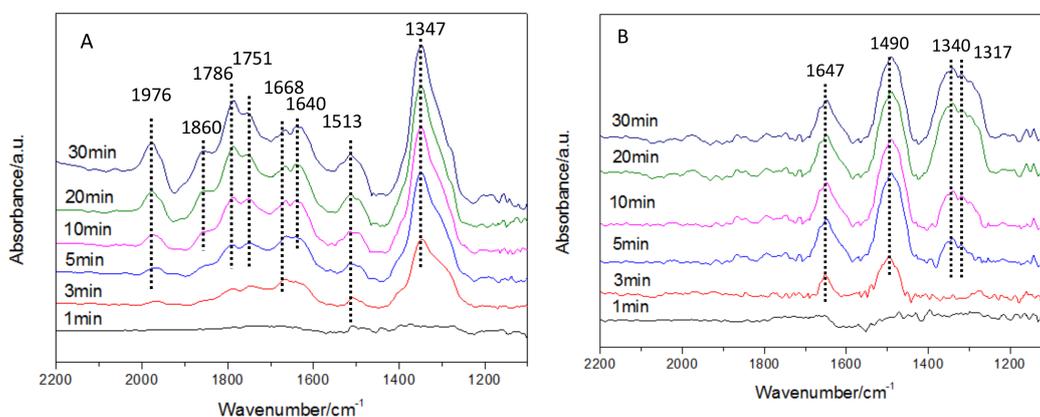


Figure 3. DRIFT spectra for $\text{NO} + \text{O}_2$ adsorption at $250\text{ }^\circ\text{C}$ on: (A) Cat-A; and (B) Cat-B.

2.2.3. $\text{NO} + \text{O}_2$ Adsorption on the Surface of the Catalysts after NH_3 Pre-Adsorption

The reaction of $\text{NO} + \text{O}_2$ with pre-adsorbed NH_3 at $250\text{ }^\circ\text{C}$ on the surface of both catalysts was investigated using DRIFT to understand the reactivity of NH_3 adsorbed on the catalysts. As seen in Figure 4A, several peaks that correspond to coordinated NH_3 (L) and NH_4^+ (B) species on the surface of Cat-A are observed. When $\text{NO} + \text{O}_2$ was added, Lewis and Brønsted acidity decreased gradually within 10 min, and, after 20 min, several bands (1349 , 1514 , 1638 , 1786 , and 1944 cm^{-1}) that correspond to adsorbed NO_x species appeared and grew with time. The adsorption behaviors of Cat-B (Figure 4B) were similar to those of Cat-A. Over time, all of the peaks gradually disappeared, accompanied by the appearance of nitrate species. These results imply that coordinated NH_3 and NH_4^+ species participate in the NH_3 -SCR reaction and that both were active species.

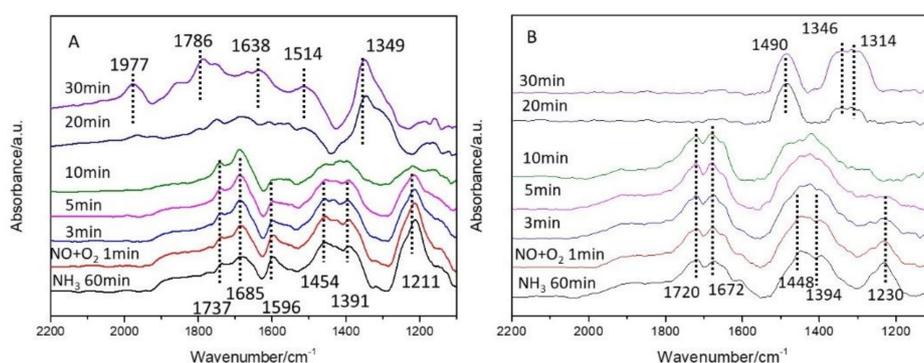


Figure 4. DRIFT spectra of $\text{NO} + \text{O}_2$ reacted with pre-adsorbed NH_3 species at $250\text{ }^\circ\text{C}$ on: (A) Cat-A; and (B) Cat-B.

2.2.4. NH_3 Adsorption on the Surface of the Catalysts after $\text{NO} + \text{O}_2$ Pre-Adsorption

The catalysts were pre-treated with $\text{NO} + \text{O}_2$ at $250\text{ }^\circ\text{C}$ for 60 min, and then NH_3 was introduced to investigate the reaction of NH_3 with nitrate species over the catalysts. As seen in Figure 5A, several peaks that correspond to nitrate species were found in the spectra after treatment with $\text{NO} + \text{O}_2$. With the introduction of NH_3 , the amounts of free nitrate ions (1347 cm^{-1}), bidentate nitrates

(1513 cm^{-1}), NO_2 (1640 cm^{-1}), and N_2O_4 (1668 cm^{-1}) decreased quickly within 1 min. Surface NO (1840 cm^{-1}) and NOH^+ (1976 cm^{-1}) in the Keggin structure gradually decreased in 5 min, implying that NO in the secondary structure of Keggin anions participates in the reaction. However, the peak at 1786 cm^{-1} , which corresponds to $\text{trans}(\text{NO})_2$, is still present after purging with NH_3 for 30 min, and this suggests that the Eley–Rideal (E-R) mechanism occurred [26]. For Cat-B (Figure 5B), a series of peaks that correspond to nitrate species were observed in the spectra. After NH_3 was introduced for 1 min, NO_2 (1647 cm^{-1}) disappeared, and this can enhance the process of the “fast-SCR” reaction. Compared with Cat-A, free nitrate ions of Cat-B decreased more slowly and monodentate nitrates disappeared gradually within 5 min. It has been reported that monodentate nitrates and NO_2 molecules had higher activity in the SCR reaction than free nitrate ions. In our results, free nitrate ions for Cat-A, which had the Keggin structure, also easily participated in the reaction, and this was possibly because NO_x was trapped by the NH_4^+ of the Keggin structure in free nitrate ions, such as in the case of NO_x storage/reduction (NSR) catalysts where NO_x can easily be trapped.

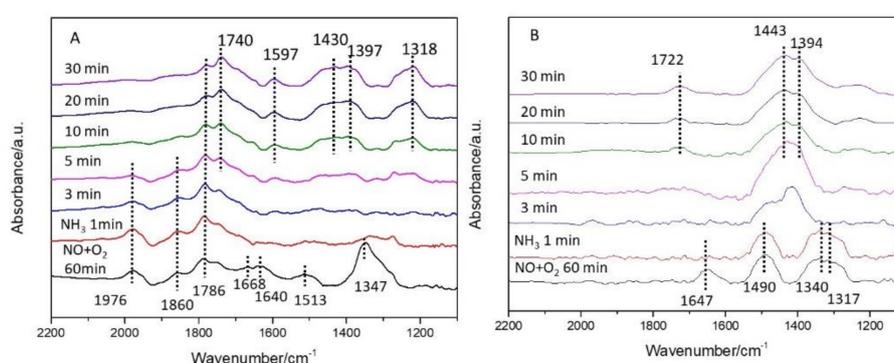


Figure 5. DRIFT spectra of NH_3 reacted with pre-adsorbed $\text{NO} + \text{O}_2$ species at 250 °C on: (A) Cat-A; and (B) Cat-B.

2.3. Effect of NH_4^+ in $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}$ for NH_3 -SCR

It is known that NH_3 adsorption and storage is important for NH_3 -SCR [33,34]. Compared with oxide SCR catalysts, Cat-A, which has the Keggin structure, has many NH_4^+ ions. Moffat et al. reported that NH_4^+ of ammonium 12-tungstophosphate can interact with NO_2 and NO and can be regenerated from ammonia gas at 150 °C [9]. Hence, it is essential to know whether NH_4^+ of the Keggin structure participates in NH_3 -SCR and if NH_4^+ can be regenerated for Cat-A.

If NH_4^+ of the Keggin structure participates in the reaction, the SCR reaction on Cat-A would continue longer than that on Cat-B without NH_3 . To verify this assumption, NO conversion of Cat-A and Cat-B after cutting off NH_3 was investigated, and the results are shown in Figure 6. As seen in Figure 6, NO conversions on the two catalysts decreased after cutting off NH_3 . For Cat-A, NO conversion remained 100% for 14 min, whereas NO conversion over Cat-B kept remained 100% for only 4 min. Thus, it is obvious that Cat-A, which has the Keggin structure, had higher NH_3 storage than Cat-B, and this suggests that NH_4^+ of the Keggin structure participates in the reaction.

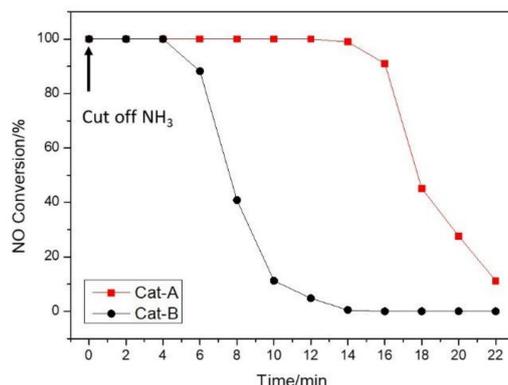


Figure 6. NO conversion of Cat-A and Cat-B over time after cutting off NH_3 . Reaction conditions: $T = 250\text{ }^\circ\text{C}$, $[\text{NO}] = 1000\text{ ppm}$, $[\text{O}_2] = 5\%$, $\text{GHSV} = 40,000\text{ h}^{-1}$, and N_2 balance gas.

Change in the Keggin structure during successive adsorption of $\text{NO} + \text{O}_2$ and NH_3 was investigated using FT-IR spectra to further verify participation of NH_4^+ in the SCR reaction. As seen in Figure 7, vibrational bands for NH_4^+ , P-O, and Mo-O-Mo in the Keggin structure are observed at 1402 , 1062 , and 906 cm^{-1} , respectively. After adsorption of NO , the peak at 1402 cm^{-1} disappeared. NH_3 was added after cutting off $\text{NO} + \text{O}_2$, and the peak at 1402 cm^{-1} reappeared. Moreover, the peaks at 1062 and 906 cm^{-1} remained stable during the whole reaction process, and this suggests that HPAs did not change during the reaction. Thus, it was determined that NH_4^+ of the Keggin structure participates in the SCR reaction and was regenerated from ammonia gas. Meanwhile, the Keggin structure (of the HPAs) was unchanged in the reaction. In situ Raman spectra of Cat-A were recorded (Figure S4) to further study the stability of the Keggin structure in the SCR reaction. The results indicate that the peaks corresponding to the Keggin structure did not shift, and this suggests that there was no structural perturbation during the reaction.

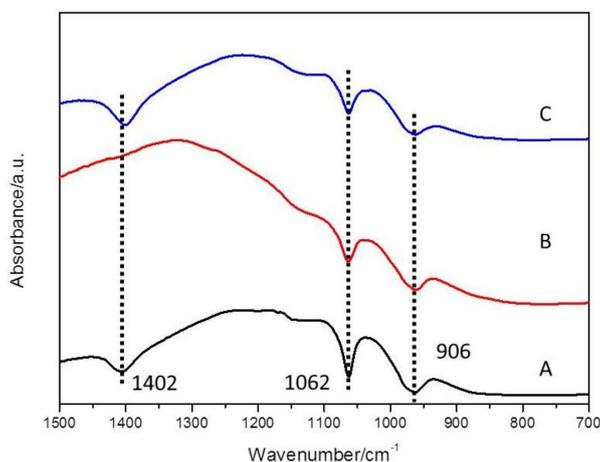


Figure 7. FT-IR spectra of Cat-A with: (A) no adsorption; (B) adsorption of $\text{NO} + \text{O}_2$; and (C) after cutting off $\text{NO} + \text{O}_2$, adsorption of NH_3 .

2.4. Reaction Mechanism

From DRIFT spectra for NH_3 adsorption on the two samples, it is observed that NH_3 was adsorbed on Brönsted and Lewis acid sites in the forms of NH_4^+ and NH_3 , respectively. After $\text{NO} + \text{O}_2$ was passed over the catalyst surface that was pretreated with NH_3 , the adsorbed NH_3 species gradually vanished in 10 min, and this indicates that both Brönsted and Lewis acid sites were active centers. As shown in DRIFT spectra of $\text{NO} + \text{O}_2$ adsorption, NO was adsorbed and oxidized to NO_2 and other

nitrate species on the two samples. There were more kinds of NO_x species adsorbed on Cat-A than on Cat-B. Different results were observed when NH_3 was passed over the surface of each of the two samples that were pretreated with $\text{NO} + \text{O}_2$ at 250°C . Compared with Cat-B, not all of the adsorbed NO_x species participated in the reaction over Cat-A, and most of the adsorbed NO_x species quickly vanished in 1 min, which indicates that both the E-R and L-H mechanisms occurred [35–38]. Noticeably, the peaks of NOH^+ disappeared after 5 min, and this suggests that NO in the secondary structure of the Keggin anions (NOH^+) also participated in reaction. The effect of NH_4^+ in the Keggin structure for the SCR reaction was investigated, and the results reveal that NH_4^+ of the Keggin structure participates in the SCR reaction as an NH_3 pool and can be regenerated from ammonia gas.

Based on the above discussion, a mechanism for improving the low-temperature activity of Cat-A was proposed; the proposed mechanism is shown in Figure 8 and is described as follows.

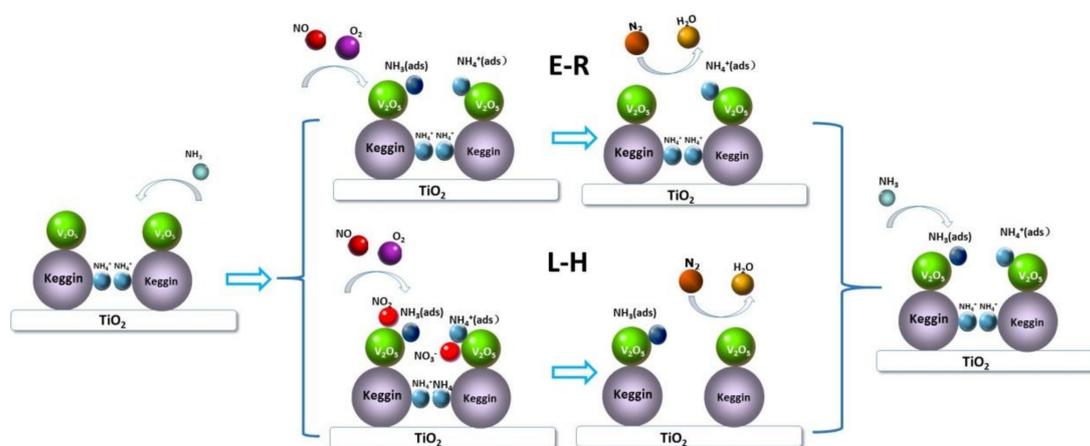


Figure 8. Schematic of the proposed NH_3 -SCR reaction mechanism over Cat-A.

Both the E-R and L-H mechanisms occurred in the NH_3 -SCR reaction. For the E-R mechanism, NH_3 was adsorbed on Lewis acid sites and reacted directly with gaseous NO and NO_2 . This was followed by decomposition into N_2 and H_2O . For the L-H mechanism, NO was adsorbed, and then most of it was oxidized to nitrate species (NO_3^- and NO_2 -adsorbed), which reacted with NH_3 -adsorbed species. It is noted that the catalyst with Keggin structure had more Brönsted acid Lewis acid sites than the catalyst with oxide phase. In addition, NH_4^+ of the Keggin structure reacted by the L-H mechanism and was regenerated during the reaction; thus, low-temperature SCR activity was promoted via the L-H mechanism.

For Cat-B, the mechanisms were similar to Cat-A. Both the E-R and L-H mechanisms also occurred in the reaction. For the E-R mechanism, gaseous NO and NO_2 could react with NH_3 on Lewis acid sites. For the L-H mechanism, NO could be adsorbed and then oxidized to nitrate species. Most of the nitrate species were monodentate nitrates and NO_2 -adsorbed not free NO_3^- , and the nitrate species could react with NH_3 -adsorbed species. The results were in agreement with many SCR catalysts with oxide phase [25,26,39].

3. Experimental

3.1. Catalyst Preparation

Two kinds of catalysts were prepared via impregnation, and the main chemical compositions were the same. Specifically, $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ loading was 20 wt % and V_2O_5 loading was 1 wt %.

The catalyst with the Keggin structure was prepared as follows. $\text{NH}_4\text{H}_2\text{PO}_4$ (0.6 g, Fuchen, Tianjin, China, 99%) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ (11.5 g, Fuchen, Tianjin, China, 99%) were dissolved in distilled water (100 mL). Solution pH was adjusted to a value of about 1. TiO_2 anatase powder (40.0 g, Xinhua,

Chongqing, China, 99%) was added to the precursor solution and solid to liquid ratio (g/mL) was 2:5. The mixture was stirred at 80 °C for 5 h and then dried at 120 °C for 3 h. The solid was ground into a powder and calcined at 400 °C for 5 h. NH_4VO_3 (0.6 g, Fuchen, Tianjin, China, 99%) was then added to a solution of oxalic acid, and the weight of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Fuchen, Tianjin, China, 99%) was double that of NH_4VO_3 . Desiccation and calcination conditions were the same as above, and the obtained catalyst was denoted as Cat-A.

Catalysts with an oxide phase were prepared via multiple impregnation methods to avoid generating the Keggin structure. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ (11.5 g) was dissolved in 100 mL of distilled water. TiO_2 anatase powder was impregnated with the precursor solution and stirred at 80 °C for 5 h. The mixture was then dried at 120 °C and was calcined at 400 °C for 5 h. $\text{NH}_4\text{H}_2\text{PO}_4$ (0.6 g) was then dissolved in 100 mL of distilled water. V_2O_5 was loaded using the above conditions, and this sample was denoted as Cat-B.

3.2. Catalytic Activity Test

Catalytic activities of the samples were measured in a fixed bed quartz reactor (9 mm i.d.) with 0.4 mL of catalysts (40–60 mesh). Typical reactant gas was a mixture of 1000 ppm NO, 1000 ppm NH_3 , 5% O_2 , 5% water vapor, and 350 ppm SO_2 with a balance of N_2 under a flow of 500 mL/min. The space velocity was $40,000 \text{ h}^{-1}$. Concentrations of NO and NH_3 were continuously detected using a Thermo Scientific 17i NO_x chemiluminescence analyzer. N_2O was monitored using a Bruker Tensor 27 FTIR spectrometer. The reaction system was maintained at each reaction temperature for 30 min before analysis. The equations used to calculate NO_x conversion and N_2 selectivity are as follows:

$$\text{NO conversion}(\%) = \frac{[\text{NO}]_{\text{in}} - ([\text{NO}]_{\text{out}} + [\text{NO}_2]_{\text{out}})}{[\text{NO}]_{\text{in}}} \times 100\% \quad (1)$$

$$\text{N}_2 \text{ selectivity}(\%) = \left(1 - \frac{[\text{NO}_2]_{\text{out}} + 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NH}_3]_{\text{in}} + [\text{NO}]_{\text{in}} - [\text{NH}_3]_{\text{out}} - [\text{NO}]_{\text{out}}} \right) \times 100\% \quad (2)$$

4. Conclusions

Two kinds of catalysts (one with and one without the Keggin structure) are synthesized to investigate the effect of the Keggin structure on the NH_3 -SCR reaction. Cat-A, which had the Keggin structure, exhibits better low-temperature SCR performance. NH_3 is adsorbed on both Brönsted and Lewis acid sites over the two catalysts but the catalyst with Keggin structure has more Brönsted and Lewis acid sites. Moreover, there are more kinds of adsorbed NO_x species on Cat-A than on Cat-B, and the adsorbed NO_x species are mainly free nitrate ions. The two catalysts follow both E-R and L-H mechanisms. Compared with Cat-B, most of the adsorbed NO_x species for Cat-A react quickly with gaseous NH_3 . In addition, NH_4^+ of the Keggin structure participates in the reaction via the L-H mechanism and is recovered by ammonia gas in the flow. Thereby, more acid sites are provided, adsorbed NO_x species activity is improved, and more NH_4^+ ions participate in the L-H mechanism over Cat-A, which had the Keggin structure, thus promoting SCR activity.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/8/4/143/s1>, Characterization methods: XRD and Raman results (Figures S1 and S2); compositions and BET surface areas of Cat-A and Cat-B (Table S1); NH_3 -TPD results (Figure S3); in situ sequential Raman spectra results (Figure S4); the time-on-stream stability of the catalysts (Figure S5).

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Author Contributions: Rui Wu and Hong He conceived and designed the experiments; Rui Wu experiments; Rui Wu, Ningqiang Zhang and Wenge Qu analyzed the data; Liyun Song and Lingcong Li contributed analysis tools; Rui Wu wrote the paper.

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

References

1. Amiridis, M.D.; Duevel, R.V.; Wachs, I.E. The effect of metal oxide additives on the activity of V_2O_5/TiO_2 catalysts for the selective catalytic reduction of nitric oxide by ammonia. *Appl. Catal. B Environ.* **1999**, *20*, 111–122. [[CrossRef](#)]
2. Busca, G.; Lietti, L.; Ramis, G.; Berti, F. Chemical and mechanistic aspects of the selective catalytic reduction of NO_x by ammonia over oxide catalysts: A review. *Appl. Catal. B Environ.* **1998**, *18*, 1–36. [[CrossRef](#)]
3. Li, P.; Liu, Q.; Liu, Z. Behaviors of NH_4HSO_4 in SCR of NO by NH_3 over different cokes. *Chem. Eng. J.* **2012**, *181–182*, 169–173. [[CrossRef](#)]
4. Kamata, H.; Takahashi, K.; Odenbrand, C.I. Surface acid property and its relation to SCR activity of phosphorus added to commercial $V_2O_5 (WO_3)/TiO_2$ catalyst. *Catal. Lett.* **1998**, *53*, 65–71. [[CrossRef](#)]
5. Putluru, S.S.R.; Schill, L.; Godiksen, A.; Poreddy, R.; Mossin, S.; Jensen, A.D.; Fehrmann, R. Promoted V_2O_5/TiO_2 catalysts for selective catalytic reduction of NO with NH_3 at low temperatures. *Appl. Catal. B Environ.* **2016**, *183*, 282–290. [[CrossRef](#)]
6. Hill, C.L. Foreword: Polyoxometalates in catalysis. *J. Mol. Catal. A Chem.* **1996**, *114*, 1. [[CrossRef](#)]
7. Chen, Y.; Wang, Y.; Lu, J.; Wu, C. The viscosity reduction of nano-keggin- $K_3PMo_{12}O_{40}$ in catalytic aquathermolysis of heavy oil. *Fuel* **2009**, *88*, 1426–1434. [[CrossRef](#)]
8. Mizuno, N.; Misono, M. Heterogeneous catalysis. *Chem. Rev.* **1998**, *98*, 199–218. [[CrossRef](#)] [[PubMed](#)]
9. Bélanger, R.; Moffat, J.B. The sorption and reduction of nitrogen oxides by 12-tungstophosphoric acid and its ammonium salt. *Catal. Today* **1998**, *40*, 297–306. [[CrossRef](#)]
10. Yang, R.T.; Chen, N. A new approach to decomposition of nitric oxide using sorbent/catalyst without reducing gas: Use of heteropoly compounds. *Ind. Eng. Chem. Res.* **1994**, *33*, 825–831. [[CrossRef](#)]
11. Vaezzadeh, K.; Petit, C.; Pitchon, V. The removal of NO_x from a lean exhaust gas using storage and reduction on $H_3PW_{12}O_{40} \cdot 6H_2O$. *Catal. Today* **2002**, *73*, 297–305. [[CrossRef](#)]
12. Yoshimoto, R.; Ninomiya, T.; Okumura, K.; Niwa, M. Cooperative effect induced by the mixing of Na-ZSM-5 and $Pd/H_3PW_{12}O_{40}/SiO_2$ in the selective catalytic reduction of NO with aromatic hydrocarbons. *Appl. Catal. B Environ.* **2007**, *75*, 175–181. [[CrossRef](#)]
13. Putluru, S.S.R.; Jensen, A.D.; Riisager, A.; Fehrmann, R. Heteropoly acid promoted V_2O_5/TiO_2 catalysts for NO abatement with ammonia in alkali containing flue gases. *Catal. Sci. Technol.* **2011**, *1*, 631–637. [[CrossRef](#)]
14. Weng, X.; Dai, X.; Zeng, Q.; Liu, Y.; Wu, Z. DRIFT studies on promotion mechanism of $H_3PW_{12}O_{40}$ in selective catalytic reduction of NO with NH_3 . *J. Colloid Interface Sci.* **2016**, *461*, 9–14. [[CrossRef](#)] [[PubMed](#)]
15. Lietti, L.; Nova, I.; Ramis, G.; Dall'Acqua, L.; Busca, G.; Giamello, E.; Forzatti, P.; Bregani, F. Characterization and Reactivity of $V_2O_5-MoO_3/TiO_2$ De- NO_x SCR Catalysts. *J. Catal.* **1999**, *187*, 419–435. [[CrossRef](#)]
16. Ettireddy, P.R.; Ettireddy, N.; Boningari, T.; Pardemann, R.; Smirniotis, P.G. Investigation of the selective catalytic reduction of nitric oxide with ammonia over Mn/TiO_2 catalysts through transient isotopic labeling and in situ FT-IR studies. *J. Catal.* **2012**, *292*, 53–63. [[CrossRef](#)]
17. Song, Z.; Zhang, Q.; Ma, Y.; Liu, Q.; Ning, P.; Liu, X.; Wang, J.; Zhao, B.; Huang, J.; Huang, Z. Mechanism-dependent on the different CeO_2 supports of phosphotungstic acid modification CeO_2 catalysts for the selective catalytic reduction of NO with NH_3 . *J. Taiwan Inst. Chem. E* **2017**, *71*, 277–284. [[CrossRef](#)]
18. Yao, X.; Zhang, L.; Li, L.; Liu, L.; Cao, Y.; Dong, X.; Gao, F.; Deng, Y.; Tang, C.; Chen, Z.; et al. Investigation of the structure, acidity, and catalytic performance of $CuO/Ti_{0.95}Ce_{0.05}O_2$ catalyst for the selective catalytic reduction of NO by NH_3 at low temperature. *Appl. Catal. B Environ.* **2014**, *150–151*, 315–329. [[CrossRef](#)]
19. Thirupathi, B.; Smirniotis, P.G. Co-doping a metal (Cr, Fe, Co, Ni, Cu, Zn, Ce, and Zr) on Mn/TiO_2 catalyst and its effect on the selective reduction of NO with NH_3 at low-temperatures. *Appl. Catal. B Environ.* **2011**, *110*, 195–206. [[CrossRef](#)]
20. You, Y.; Chang, H.; Zhu, T.; Zhang, T.; Li, X.; Li, J. The poisoning effects of phosphorus on CeO_2-MoO_3/TiO_2 DeNO_x catalysts: NH_3 -SCR activity and the formation of N_2O . *Mol. Catal.* **2017**, *439*, 15–24. [[CrossRef](#)]
21. Zeng, Y.; Zhang, S.; Wang, Y.; Zhong, Q. CeO_2 supported on reduced TiO_2 for selective catalytic reduction of NO by NH_3 . *J. Colloid Interface Sci.* **2017**, *496*, 487–495. [[CrossRef](#)] [[PubMed](#)]
22. Li, W.; Oshihara, K.; Ueda, W. Catalytic performance for propane selective oxidation and surface properties of 12-molybdophosphoric acid treated with pyridine. *Appl. Catal. A Gen.* **1999**, *182*, 357–363. [[CrossRef](#)]

23. Boningari, T.; Ettireddy, P.R.; Somogyvari, A.; Liu, Y.; Vorontsov, A.; McDonald, C.A.; Smirniotis, P.G. Influence of elevated surface texture hydrated titania on Ce-doped Mn/TiO₂ catalysts for the low-temperature SCR of NO_x under oxygen-rich conditions. *J. Catal.* **2015**, *325*, 145–155. [[CrossRef](#)]
24. Pappas, D.K.; Boningari, T.; Boolchand, P.; Smirniotis, P.G. Novel manganese oxide confined interweaved titania nanotubes for the low-temperature Selective Catalytic Reduction (SCR) of NO_x by NH₃. *J. Catal.* **2016**, *334*, 1–13. [[CrossRef](#)]
25. Liu, Z.; Zhang, S.; Li, J.; Ma, L. Promoting effect of MoO₃ on the NO_x reduction by NH₃ over CeO₂/TiO₂ catalyst studied with in situ DRIFTS. *Appl. Catal. B Environ.* **2014**, *144*, 90–95. [[CrossRef](#)]
26. Liu, J.; Li, X.; Zhao, Q.; Ke, J.; Xiao, H.; Lv, X.; Liu, S.; Tadé, M.; Wang, S. Mechanistic investigation of the enhanced NH₃-SCR on cobalt-decorated Ce-Ti mixed oxide: In situ FTIR analysis for structure-activity correlation. *Appl. Catal. B Environ.* **2017**, *200*, 297–308. [[CrossRef](#)]
27. Valyon, J.; Hall, W. Surface Species Formed from NO on Copper Zeolites. *ChemInform* **1993**, *24*. [[CrossRef](#)]
28. Herring, A.M.; McCormick, R.L. In situ infrared study of the absorption of nitric oxide by 12-tungstophosphoric acid. *J. Phys. Chem. B* **1998**, *102*, 3175–3184. [[CrossRef](#)]
29. Chen, L.; Li, J.; Ge, M. DRIFT Study on Cerium–Tungsten/Titania Catalyst for Selective Catalytic Reduction of NO_x with NH₃. *Environ. Sci. Technol.* **2010**, *44*, 9590–9596. [[CrossRef](#)] [[PubMed](#)]
30. Li, Z.; Li, J.; Liu, S.; Ren, X.; Ma, J.; Su, W.; Peng, Y. Ultra hydrothermal stability of CeO₂-WO₃/TiO₂ for NH₃-SCR of NO compared to traditional V₂O₅-WO₃/TiO₂ catalyst. *Catal. Today* **2015**, *258*, 11–16. [[CrossRef](#)]
31. Toops, T.J.; Smith, D.B.; Epling, W.S.; Parks, J.E.; Partridge, W.P. Quantified NO_x adsorption on Pt/K/gamma-Al₂O₃ and the effects of CO₂ and H₂O. *Appl. Catal. B Environ.* **2005**, *58*, 255–264. [[CrossRef](#)]
32. Büchel, R.; Strobel, R.; Baiker, A.; Pratsinis, S.E. Flame-Made Pt/K/Al₂O₃ for NO_x Storage–Reduction (NSR) Catalysts. *Top. Catal.* **2009**, *52*, 1799–1802. [[CrossRef](#)]
33. Kamasamudram, K.; Currier, N.W.; Chen, X.; Yezerets, A. Overview of the practically important behaviors of zeolite-based urea-SCR catalysts, using compact experimental protocol. *Catal. Today* **2010**, *151*, 212–222. [[CrossRef](#)]
34. Schmieg, S.J.; Oh, S.H.; Kim, C.H.; Brown, D.B.; Lee, J.H.; Peden, C.H.F.; Kim, D.H. Thermal durability of Cu-CHA NH₃-SCR catalysts for diesel NO_x reduction. *Catal. Today* **2012**, *184*, 252–261. [[CrossRef](#)]
35. Ramis, G.; Bregani, F.; Forzatti, P. Fourier transform-infrared study of the adsorption and coadsorption of nitric oxide, nitrogen dioxide and ammonia on vanadia-titania and mechanism of selective catalytic reduction. *Appl. Catal.* **1990**, *64*, 259–278. [[CrossRef](#)]
36. Topsøe, N.-Y. Characterization of the nature of surface sites on vanadia-titania catalysts by FTIR. *J. Catal.* **1991**, *128*, 499–511. [[CrossRef](#)]
37. Lietti, L.; Svachula, J.; Forzatti, P.; Ramis, G.; Bregani, P. Surface and catalytic properties of Vanadia-Titania and Tungsta-Titania systems in the Selective Catalytic Reduction of nitrogen oxides. *Catal. Today* **1993**, *17*, 131–139. [[CrossRef](#)]
38. Topsøe, N.-Y. Mechanism of the selective catalytic reduction of nitric oxide by ammonia elucidated by in situ on-line Fourier transform infrared spectroscopy. *Science* **1994**, *265*, 1217–1219. [[CrossRef](#)] [[PubMed](#)]
39. Peng, Y.; Li, K.; Li, J. Identification of the active sites on CeO₂-WO₃ catalysts for SCR of NO_x with NH₃: An in situ IR and Raman spectroscopy study. *Appl. Catal. B Environ.* **2013**, *140*, 483–492. [[CrossRef](#)]

