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Inhibitory role of excessive NH_3 in NH_3 -SCR on CeWO_x at low temperatures

An inhibitory effect of excessive NH_3 on NH_3 -SCR over a CeWO_x catalyst at low temperatures was found, and H_2O can depress the inhibitory effect on standard SCR reaction. Excessive NH_3 can inhibit the standard and fast SCR by blocking the sites for NO adsorption and facilitating the formation of NH_4NO_3 , respectively.

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Inhibitory role of excessive NH₃ in NH₃-SCR on CeWO_x at low temperatures†

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An inhibitory role of excessive NH₃ at low temperatures in the selective catalytic reduction of NO_x with NH₃ over CeWO_x was revealed and studied comprehensively, both in the presence and absence of H₂O. For the first time, an inhibitory effect of NH₃ on NO adsorption over CeWO_x has been found.

Currently, the removal of nitrogen oxides (NO_x) from diesel engine exhaust remains a challenge. To this aim, the selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) has been confirmed to be an effective way of NO_x abatement. In addition to zeolite catalysts,^{1–3} non-toxic vanadium-free oxide catalysts have been gaining much attention due to their environmentally friendly properties and excellent NH₃-SCR performance over a wide temperature range, *e.g.* Fe-containing mixed oxides^{4–6} and Ce-containing mixed oxides.^{7–12} CeO₂ has been proven to be efficient not only as a promoter or support for NH₃-SCR,^{13–16} but also as an active component of catalysts above 200 °C.^{17–21} By means of a simple homogeneous precipitation method, our group has reported the preparation of a promising CeWO_x catalyst for NH₃-SCR.¹⁹ Even at a high gas hourly space velocity (GHSV) (500 000 h^{–1}), this catalyst exhibits excellent activity, achieving ~100% NO_x conversion within a wide temperature range (250–425 °C). Therefore, revealing the NH₃-SCR mechanism over this CeWO_x catalyst in detail is of considerable importance.

In our previous report, the formation of greater amounts of surface nitrates was suggested to be important for

obtaining high NH₃-SCR performance.²² Even though NH₃ serves as a reductant for NH₃-SCR, its role in this reaction is under debate. Some authors proposed that NH₃ plays a negative role in the NH₃-SCR reaction,^{23–26} whereas others suggested that the effect of NH₃ was negligible.^{27–30} Grossale *et al.*²³ pointed out that NH₃ could inhibit the reaction between surface nitrates and NO on Fe-ZSM-5, which could produce nitrites that would react with the adsorbed NH₃ to produce H₂O and N₂. Nova *et al.*²⁴ reported that NH₃ has an inhibitory effect on the standard SCR reaction over V₂O₅-WO₃/TiO₂, due to the blockage of the redox sites for NO + NH₃ activation by NH₃ adsorption. Odenbrand *et al.*²⁷ reported that the NH₃ concentration dependence was negligible in NH₃-SCR over a catalyst containing V₂O₅-WO₃/TiO₂ and sepiolite. Similarly, Li *et al.*²⁸ found that the reaction order of NH₃ was almost zero during standard SCR over Fe-Mo/ZSM-5, indicating that the surface of the catalyst was covered completely by NH₃ during the reaction. Similar conclusions have been drawn for the NH₃-SCR reaction over Fe-ZSM-5 (ref. 29) and Cu-ZSM-5.³⁰ The effect of NH₃ seems to be different over different kinds of catalysts. Since this difference could be closely related to the different mechanisms of NH₃-SCR, further investigation on the effects of NH₃ can offer more information for the study of the reaction mechanism. However, knowledge on the effect of the NH₃ concentration on standard or fast SCR over CeWO_x is still lacking so far.

In the present study, the effect of H₂O on the role of NH₃ was investigated. The presence of competitive adsorption between NO and NH₃ was confirmed, and for the first time, the inhibitory effects of excessive NH₃ at low temperatures on the standard and fast SCR reactions over CeWO_x were investigated comprehensively. In addition, it was found that the inhibitory role of NH₃ on the standard SCR was insignificant in the presence of H₂O at low temperatures.

To determine the effect of H₂O on the role of excessive NH₃ during the standard and fast SCR over CeWO_x, the NO_x conversion as a function of the reaction temperature in 500

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ppm and 1000 ppm NH_3 in the absence and presence of H_2O was obtained, as shown in Fig. 1. It is apparent that more NH_3 in the feed resulted in lower NO_x conversion below 250 °C during either standard or fast SCR in the absence of H_2O , as well as during the fast SCR in the presence of H_2O . However, increasing the NH_3 content to 1000 ppm in the gas feed did not change the NO_x conversion below 250 °C during the standard SCR in the presence of H_2O .

In order to clarify whether the adsorbed NH_3 prohibited the adsorption of NO , a transient response method (TRM)^{31,32} was applied (see the ESI†) and the following experiments were conducted. CeWO_x was first saturated with NH_3 and then purged with N_2 . Afterwards, NO was introduced into the reactor, and the results are shown in Fig. S1a.† NO could not adsorb on the NH_3 -presorbed CeWO_x in the absence of H_2O and no NH_3 was removed, indicating that the pre-adsorbed NH_3 inhibited the adsorption of NO at room temperature in the absence of H_2O . In order to study whether the adsorbed NH_3 prohibited the adsorption of NO in the presence of H_2O , CeWO_x was first saturated with H_2O and NH_3 and then purged with N_2 . Then, a mixture of NO

and H_2O was introduced. As shown in Fig. S1b,† NO could adsorb on the H_2O - and NH_3 -presorbed CeWO_x . However, the amount of NO adsorbed ($\sim 14 \mu\text{mol g}^{-1}$) was lower than that on the fresh catalyst ($\sim 20 \mu\text{mol g}^{-1}$) (Table S1†). Interestingly, desorption of NH_3 was observed simultaneously during this process, which is different from the results in the absence of H_2O , indicating that some weakly adsorbed NH_3 could be removed by NO at 30 °C, and competitive adsorption between NH_3 and NO possibly occurred on CeWO_x at 30 °C since NO could adsorb on the surface of the catalyst only after NH_3 desorbed.

In order to clarify whether the adsorbed NO inhibited the NH_3 adsorption, CeWO_x was first saturated with NO and then purged with N_2 at room temperature. Then, NH_3 was introduced onto the surface of the CeWO_x . It can be seen that in the absence of H_2O , the amount of NH_3 adsorbed did not decrease dramatically, as shown in Fig. S2 and Table S1.† As shown in our previous report,³¹ the amount of NH_3 adsorbed on NO - and H_2O -pre-treated CeWO_x was $\sim 245 \mu\text{mol g}^{-1}$, and the pre-adsorption of NO and H_2O did not decrease the amount of NH_3 subsequently adsorbed at 30 °C ($\sim 243 \mu\text{mol g}^{-1}$) (Fig. S2b and Table S1†). It was reported that in the presence of H_2O , NO molecules were weakly adsorbed and could be easily removed by N_2 purging,³¹ and thus, a very small amount of NO ($< 4 \mu\text{mol g}^{-1}$) remained on the surface of CeWO_x after N_2 purging, resulting in no detectable decrease in the amount of subsequently adsorbed NH_3 . In the absence of H_2O , it can be proposed that $\sim 10 \mu\text{mol g}^{-1}$ nitrates were formed.^{22,31} However, these nitrates did not inhibit the NH_3 adsorption dramatically, with a decrease in the NH_3 adsorption amount by $\sim 8 \mu\text{mol g}^{-1}$. *In situ* DRIFTS results (Fig. S3†) show that when NH_3 was introduced onto the surface of the catalyst pre-treated in NO , a peak was observed at 1305 cm^{-1} , ascribed to NH_4NO_3 ,²² demonstrating the formation of NH_4NO_3 . Therefore, some nitrates could react with NH_3 to form NH_4NO_3 . In addition, the amount of NH_3 adsorbed was ~ 16 times that of NO , and thus the inhibitory effect of NO adsorption on NH_3 adsorption was insignificant. The results above are the reasons why the inhibitory effect of NO pre-adsorption on the subsequent NH_3 adsorption was negligible.

It should be noted that in this work, competitive adsorption between NH_3 and NO was observed over CeWO_x only at room temperature, according to Fig. S1.† To identify whether competitive adsorption took place at the reaction temperature, the following experiment was conducted at 150 °C: the standard SCR reactant gas mixture was first introduced into the reactor, and then the NH_3 gas source was shut down after 50 min. As seen in Fig. 2, after the shutdown of the NH_3 gas source, the NO concentration first decreased, and then increased to ~ 500 ppm after reaching the minimum. Many papers reported the same phenomenon while carrying out similar experiments. Nova *et al.*²⁴ suggested that the adsorbed NH_3 blocked the active sites for $\text{NO} + \text{NH}_3$ activation, and the shutdown of the NH_3 source decreased the coverage of the adsorbed NH_3 and recovered

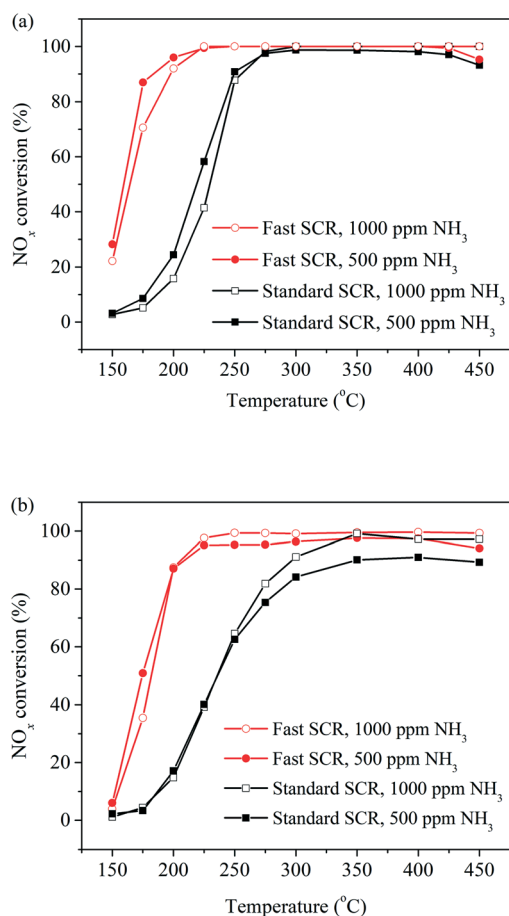


Fig. 1 NO_x conversion over CeWO_x (a) in the absence and (b) presence of H_2O . Reaction conditions: 500 ppm NO , 500 (or 1000) ppm NH_3 , 5 vol% O_2 , 5 vol% H_2O (when used) and N_2 balance for standard SCR; 250 ppm NO , 250 ppm NO_2 , 500 (or 1000) ppm NH_3 , 5 vol% O_2 , 5 vol% H_2O (when used) and N_2 balance for fast SCR.

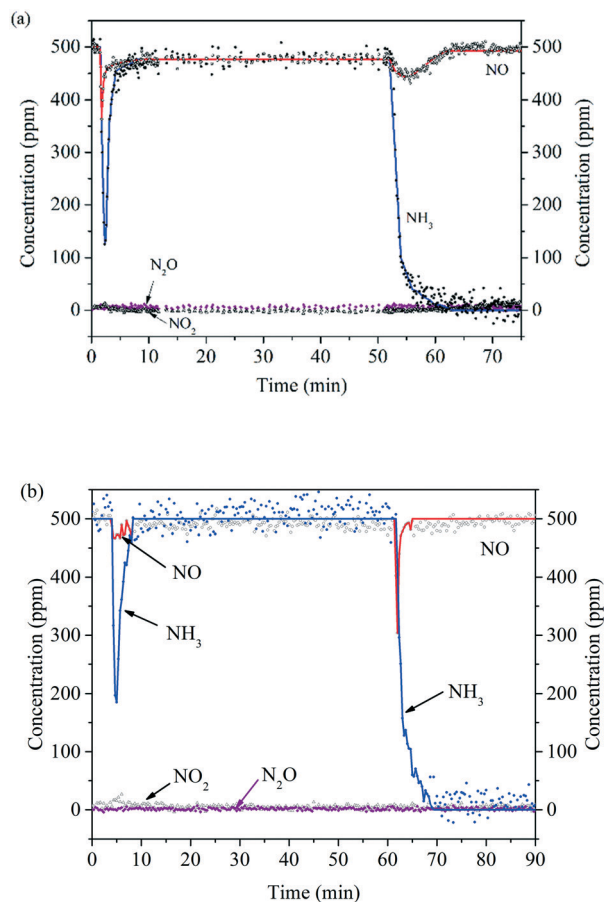


Fig. 2 Transient SCR experiments with the NH_3 feed changing from 500 ppm to 0: (a) in 500 ppm NO + 5 vol% O_2 + N_2 balance at 150 °C and (b) in 500 ppm NO + 5 vol% O_2 + 2 vol% H_2O + N_2 balance at 150 °C.

some active sites, resulting in a lower NO concentration in the gas feed. Liu *et al.*²⁵ found that there was competitive adsorption between NH_3 and NO, and the shutdown of the NH_3 source led to a decrease in the NH_3 coverage on the surface at 150 °C and an increase in the amount of adsorbed NO in the meantime, resulting in a higher NO conversion. Odriozola *et al.*²⁶ also found that the active sites for NO adsorption could be blocked by chemisorbed NH_3 . Therefore, the present experimental results shown in Fig. 2 strongly suggest the presence of competitive adsorption between NH_3 and NO at 150 °C, and the shutdown of the NH_3 source decreased the coverage of NH_3 so that more NO could be adsorbed onto the exposed active sites, leading to a decrease in the NO concentration. To investigate whether the competitive adsorption between NO and NH_3 exists at the reaction temperature in the presence of H_2O , a similar experiment was performed, *i.e.*, the standard SCR reactant gas mixture along with 2 vol% H_2O was first introduced into the reactor, and then the NH_3 gas source was shut down after 50 min at 150 °C. After the shutdown of the NH_3 gas source, the concentration of NO decreased dramatically, and then increased until levelling off after reaching its lowest point

(Fig. 2b). This phenomenon is the same as that in Fig. 2a, indicating that the competitive adsorption between NH_3 and NO occurred on CeWO_x with H_2O in the gas feed at a low reaction temperature. It should be noted that after the shutdown of the NH_3 gas source, the concentration of NO decreased more dramatically in the presence of H_2O . Since H_2O weakened the adsorption of NH_3 , it can be inferred that NH_3 desorbed faster in the presence of H_2O after the shutdown of the NH_3 source, leading to the faster exposure of the catalyst surface to NO. Thus, NO would adsorb on the catalyst surface rapidly, along with a drastic decline in the NO concentration.

It is known that NO adsorbs on the surface oxygen atoms, while NH_3 adsorbs on the acid sites. Therefore, the inhibition by NH_3 might be due to the direct blocking of the active oxygen atoms.²⁴ It is possible that the pre-adsorbed NH_3 might prevent NO from coming into contact with the surface oxygen atoms, and consequently, it is difficult for the NO gas to adsorb or react with the adsorbed NH_3 to form NH_4NO_3 . It was reported that the “nitrite path” ($[\text{Ce}^{4+}]\text{-ONO} + \text{NH}_{3(\text{ads})} \rightarrow \text{N}_2 + \text{H}_2\text{O} + [\text{Ce}^{4+}]\text{-OH}$) occurs during the standard SCR on CeWO_x at low temperatures, both in the presence and absence of H_2O .³¹ Therefore, excessive NH_3 inhibited the adsorption of NO, and further decreased the amount of $[\text{Ce}^{4+}]\text{-ONO}$. Meanwhile, the higher concentration of NH_3 would also result in the increase of the driving force for NH_3 adsorption, and the amount of the adsorbed NH_3 ($\text{NH}_{3(\text{ads})}$) would increase. The higher adsorption amount of NH_3 may somewhat compensate for the effect of lower NO adsorption. However, the effect of pre-adsorbed NO on the NH_3 adsorption was insignificant (Fig. S2†), and thus, the compensation was minor. In this way, a lower standard SCR reaction rate was obtained with excessive NH_3 (Fig. 1a). Many studies have reported the negative effects of NH_3 on the NH_3 -SCR reaction. Devadas *et al.*³³ found that at below 350 °C, NH_3 had a pronounced inhibitory effect on standard SCR over Fe-ZSM-5, leading to a decrease in NO_x conversion when NH_3 was overdosed. The authors ascribed the inhibitory effect to the competitive adsorption of NH_3 and NO_x , or to the reduction of Fe^{3+} to Fe^{2+} by NH_3 . Stevenson *et al.*³⁴ also observed a negative reaction order in NH_3 on HZSM-5, which originated from blocking of the active sites for NO oxidation by NH_3 .

For fast SCR, Grossale *et al.*²³ attributed the inhibitory effect of NH_3 on fast SCR to its reaction with NO_2 instead of the competitive chemisorption between these reactants on an Fe-zeolite catalyst. The formation of NH_4NO_3 inhibited the reaction between NO and surface nitrates, and consequently decreased the NO_x conversion. In the present study, during the fast SCR, both the “nitrite path” ($[\text{Ce}^{4+}]\text{-ONO} + \text{NH}_{3(\text{ads})} \rightarrow \text{N}_2 + \text{H}_2\text{O} + [\text{Ce}^{4+}]\text{-OH}$) and “ NH_4NO_3 path” ($\text{NO} + \text{NH}_4\text{NO}_3 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} + \text{NO}_2$) took place.³¹ An excess of NH_3 resulted in a greater amount of NH_4NO_3 , accelerating the reaction rate of the “ NH_4NO_3 path”. However, NH_4NO_3 inhibited the reaction between NO and nitrates ($\text{NO} + [\text{Ce}^{4+}]\text{-ONO}_2 \rightarrow \text{NO}_2 + [\text{Ce}^{4+}]\text{-ONO}$),²² and less nitrite ($[\text{Ce}^{4+}]\text{-ONO}$) species were

formed. Consequently, the presence of excess NH_3 decreased the reaction rate of the “nitrite path”. It is possible that the effect of the accelerated “ NH_4NO_3 path” could not compensate for the inhibition of the “nitrite path”, and thus the activity of the fast SCR was lowered by excessive NH_3 .

The amount of adsorbed NH_3 was much greater than the adsorbed NO , and it was proposed that the adsorption of NO was very important for obtaining a higher standard SCR activity over CeWO_x , at least in the low-temperature range.²² Therefore, as summarized in Fig. 3, for the standard SCR, the inhibitory role of excessive NH_3 can be ascribed to the competitive adsorption between NO and NH_3 . As for the fast SCR, the reason for the negative effect of excessive NH_3 is different from that for the standard SCR. Since surface nitrates could be formed by the adsorption of NO_2 instead of NO ,²² the amount of surface nitrates could not be reduced by the blockage due to excessive NH_3 . On the other hand, the formation of NH_4NO_3 might be one of the main reasons for the inhibitory effect of NH_3 on the fast SCR reaction.

However, it should be noted that the inhibitory role of excessive NH_3 at low temperatures on the standard SCR was negligible in the presence of H_2O , and the degree of NO conversion did not change with the increase of the NH_3 concentration (Fig. 1b). In the presence of H_2O , the inhibition of the NO adsorption by the surface-adsorbed NH_3 species also occurred, as shown in Fig. 2b. H_2O could increase the adsorption amount of NO from ~ 10 to $\sim 20 \mu\text{mol g}^{-1}$ (Table S1†) at room temperature, but $\sim 18 \mu\text{mol g}^{-1}$ of the adsorbed species were weakly adsorbed and could be removed from the surface by N_2 purging,³¹ leaving only $\sim 2 \mu\text{mol g}^{-1}$ of the adsorbed species after a N_2 purge. The amount that remained on the surface in the presence of H_2O ($< 4 \mu\text{mol g}^{-1}$) was lower than that in the absence of H_2O ($\sim 10 \mu\text{mol g}^{-1}$), which was consistent with the *in situ* DRIFTS results (Fig. S4†). Thus, most of the adsorbed NO species might not participate in the standard SCR. Consequently, it is possible that the Eley–Rideal (E–R) mechanism, in which the NO gas reacted with the adsorbed NH_3 species ($4\text{NO}_{(\text{gas})} +$

$4\text{NH}_{3(\text{ads})} + 2\text{O}_{(\text{ads})} \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$), mainly contributed to the NH_3 -SCR reaction in the presence of H_2O . In order to identify whether the Langmuir–Hinshelwood (L–H) mechanism occurred in the presence of H_2O , CeWO_x pre-treated with NO and 2 vol% H_2O was exposed to an $\text{NH}_3 + 2 \text{ vol\% } \text{H}_2\text{O}$ gas mixture at 150°C . As Fig. S5† shows, a broad peak in the range of $1500\text{--}1700 \text{ cm}^{-1}$ with a low intensity was observed after the NO adsorption, which could possibly be assigned to the nitrates formed by NO adsorption. After the NH_3 adsorption, the peaks of the surface nitrates disappeared with the appearance of NH_3 peaks (Fig. S5†), indicating that the nitrates formed by $\text{NO} + 2 \text{ vol\% } \text{H}_2\text{O}$ could react with the NH_3 gas. This result suggests that a reaction following the L–H mechanism also occurs in the presence of H_2O at 150°C . Both the E–R ($4\text{NO}_{(\text{gas})} + 4\text{NH}_{3(\text{ads})} + 2\text{O}_{(\text{ads})} \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$) and L–H ($[\text{Ce}^{4+}]\text{--ONO} + \text{NH}_{3(\text{ads})} \rightarrow \text{N}_2 + \text{H}_2\text{O} + [\text{Ce}^{4+}]\text{--OH}$) mechanisms might contribute to the NH_3 -SCR simultaneously on CeWO_x at low reaction temperatures with H_2O , as summarized in Fig. 3; thus, the competitive adsorption between NO and NH_3 might not be very important in the presence of H_2O , since the E–R mechanism was also present. It was reported in our previous study that H_2O weakened the adsorption of NH_3 , decreasing the amount of NH_3 adsorbed at 150°C .³¹ Increasing the pressure of NH_3 might result in more adsorbed NH_3 ; in this way, the reaction $4\text{NO}_{(\text{gas})} + 4\text{NH}_{3(\text{ads})} + 2\text{O}_{(\text{ads})} \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$ (E–R mechanism) was accelerated by excessive NH_3 due to the increased amount of $\text{NH}_{3(\text{ads})}$. Thus, the inhibitory effect of excessive NH_3 on the L–H mechanism would be compensated, leading to almost unchanged NO conversion at low temperatures (Fig. 1b). Also, the presence of the E–R mechanism is possibly the reason why, at higher temperatures (above 250°C), the activity was increased for higher NH_3 contents. On the other hand, at low temperatures, the decrease in the amount of NO adsorbed and the promotion of NH_3 adsorption with higher NH_3 contents led to almost unchanged NO conversion during the standard SCR in the presence of H_2O .

In summary, excessive NH_3 had an inhibitory effect on both standard and fast SCR reactions at low temperatures in the absence of H_2O . NH_3 inhibited the standard SCR by blocking the active sites for NO adsorption, whereas the negative effect of NH_3 on the fast SCR could be ascribed to its reaction with NO_2 to form NH_4NO_3 . Excessive NH_3 also had an inhibitory effect on the fast SCR reaction at low temperatures in the presence of H_2O . The effect of excessive NH_3 on the standard SCR at low temperatures was negligible, possibly due to the simultaneous presence of the L–H and E–R mechanisms. The decreased amount of NO adsorbed and the increased amount of NH_3 adsorbed in excessive NH_3 resulted in almost unchanged NO conversion at low reaction temperatures in the presence of H_2O .

Conflicts of interest

There are no conflicts to declare.

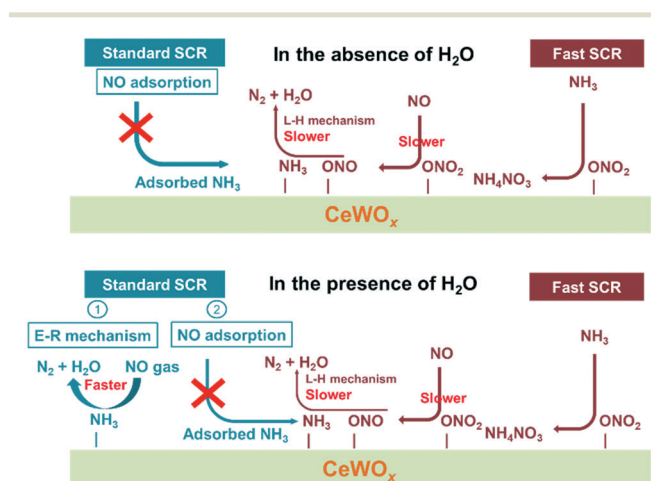


Fig. 3 Mechanism of the inhibitory effect of NH_3 on NH_3 -SCR at low temperatures.

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