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DRIFTS Study of Ammonia Activation over CaO and Sulfated CaO for NO Reduction by NH₃

XINFANG YANG, BO ZHAO,
YUQUN ZHUO,* YANG GAO,
CHANGHE CHEN, AND XUCHANG XU

Key Laboratory for Thermal Science and Power Engineering of Minister of Education, Department of Thermal Engineering, Tsinghua University, Beijing, 100084, China

CaO catalyzes NH₃ oxidation, while sulfated CaO catalyzes NO reduction by NH₃ in the presence of O₂, and the adsorption and transformation of ammonia over CaO and sulfated CaO has been investigated by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to understand their catalytic mechanism. It has been found that ammonia is first adsorbed over Lewis or Brönsted acid sites, and later undergoes hydrogen abstraction giving rise to either NH₂ amide or NH imide intermediates. The intermediates react with NO or lattice O to produce N₂ or NO. Comparing the DRIFTS of NH₃ adsorption over CaO and sulfated CaO, it is obvious that ammonia adsorbed over CaO is activated mainly in NH form apt to react with surface oxygen to produce NO, while ammonia adsorbed over sulfated CaO is activated mainly in NH₂ form apt to reduce NO. The DRIFTS results agree with experimental data and explain the catalytic mechanisms of CaO and sulfated CaO.

1. Introduction

The emission control of SO₂, NO$_x$, and trace elements such as selenium and arsenic from coal combustion has received much attention recently as these cause harm to our environment and human health. The simultaneous removal of multipollutant by calcium-based sorbent under 700−900 °C is frequently investigated to reduce emission control costs, and preliminary results indicate that this novel technology is capable of removing SO₂, NO, and trace As and Se in a single process (*1−5*). The results of flue gas desulphurization in a pilot-scale circulating fluid bed have indicated that SO₂ removal efficiency could be as high as 85%−95% when Ca/S molar ratio is 2 at 700−800 °C (*1*). At the same temperature window, the trace As and Se can also be captured by CaO (*2, 3*). Based on the calcium-based desulphurization technique, our previous work (*4, 5*) has investigated the effect of calcium-based substances on NO reduction by NH₃ in the presence of oxygen according to reaction 1 during the desulphurization process:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$
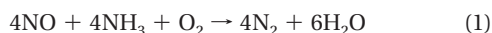
The results indicate that CaO compromises the NO reduction due to its effect of oxidizing NH₃ to NO according to reaction 2 (*6, 7*):

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (2)$$
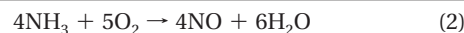
while CaO sulfation products have a positive effect on the SCR reaction (*4, 5, 8*). In the reaction system of 500 ppm NH₃ + 500 ppm NO + 5% O₂ + N₂, the conversions of NO and NH₃ at 800 °C over 5.5 g of CaO and different sulfation products of the initial 5.5 g of CaO, shown in Figure 1 (*5*), indicate the NO conversion changing with the CaO sulfation extent. At first, the NO conversion increases with the CaO conversion because of the CaO active sites (apt to catalyze NH₃ oxidation) gradually changing into the CaSO₄ active sites (apt to catalyze deNO$_x$ reaction); and then the NO conversion decreases because of the decreasing BET surface area. Also, the investigation has verified the catalytic effect of analytical grade CaSO₄ on the deNO$_x$ reaction. Combining the catalytic effect of sulfated CaO and analytical grade CaSO₄, it has been revealed that the SO₄ content in sulfated CaO plays an important role in the catalytic effect on the SCR reaction (*5*), and many studies on the sulfated metal oxide (*9−11*) have also indicated that the surface sulfated species produce acidic sites favored by ammonia adsorption, which may lead to high SCR reactivity. For NH₃ adsorption, many research studies on V₂O₅-based catalysts and other metal oxide catalysts have indicated that there are two kinds of ammonia adsorption patterns: (i) molecularly adsorbed ammonia through Lewis-type interaction on coordinatively unsaturated cations; and (ii) ammonium ions over Brönsted acidic −OH surface hydroxyl groups (*12−14*). Furthermore, the mechanism of SCR reaction has been studied and several mechanisms have been proposed (*15, 16*). However, there are few studies on the NH₃ adsorption and activation over calcium-based substances. DRIFTS study is an effective method for identifying the surface adsorbed species, and surface reaction under actual reaction conditions (*17, 18*), thus, this method is employed in this study to investigate the reaction mechanisms, which will be good for us to get full use of the catalytic effect of CaSO₄ for deNO$_x$ reaction, decrease or even avoid the negative effect from CaO, and achieve the simultaneous removal of SO₂ and NO$_x$.

In this paper, the ammonia adsorption, activation, and oxidation at different temperatures, the NO adsorption, and the SCR reaction over the catalyst under actual conditions will be investigated by DRIFTS experiments to study the SCR reaction mechanisms over sulfated CaO and the NH₃ oxidation mechanisms over CaO.
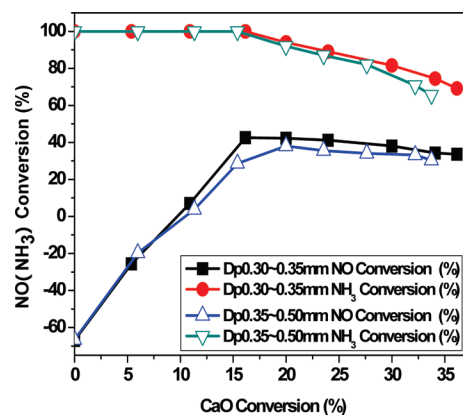

FIGURE 1. NO and NH₃ conversion over CaO with different sulfation extent in 500 ppm NH₃ + 500 ppm NO + 5% O₂ + N₂ reaction at 800 °C (D_p: initial CaO particle diameter) (*5*).

2. Experimental Section

The in situ DRIFTS experiments were carried out using Fourier transform infrared (Thermo Nicolet Corporation, NEXUS670) equipped with an MCT detector and diffuse reflectance kit accessory (HARRICK) including the praying mantis and a high temperature reaction chamber. The chamber was connected to a gas flow apparatus, which was used for passing gas over the solid samples in the sample cup of the chamber. Also, the chamber was connected to the water cooling system, which was used to control the temperature of the outer surface of the chamber and the windows during high temperature operation. In addition, the chamber was enclosed with a dome with three windows, two ZnSe windows for spectrometer radiation and one UV quartz window for viewing the sample.

Analytical grade CaO and sulfated CaO (prepared by CaO sulfation in 2000 ppm SO_2 + 5% O_2 + N_2 at 850 °C, CaO sulfation extent (X_{Ca}) was 36.5%) have been tested in the DRIFTS experiments. The CaO sulfation extent (X_{Ca}) was calculated from the mass increase of the solid sample defined in equation 3:

$$X_{Ca}(\%) = \frac{n_S}{n_{Ca}} \times 100 \qquad (3)$$

where n_S is the molar of sulfur element, and n_{Ca} is the molar of calcium element in the sulfated CaO. Before adsorption, samples were pretreated in 100 mL/min N_2 at 700 °C for 30 min to remove impurities in the sample, and then cooled to 100 °C. During the cooling process, the spectra of the sample were collected at 600, 500, 400, 300, 200, and 100 °C, which would be used as the background spectra at the corresponding temperature when collecting ammonia adsorption spectra. For ammonia adsorption under 100 °C, after pretreatment, the samples were treated with 500 ppm NH_3 + N_2 with the flow rate at 100 mL/min, and the DRIFTS were collected to identify the surface adsorbed species obtained under different adsorption times. After ammonia adsorption, the DRIFTS were also collected to identify the surface adsorbed species at different temperatures under 100 mL/min of N_2 flow using the background spectra at the corresponding temperature. Spectra were collected with the parameter of 64 scans at a resolution of 8 cm^{-1}. The procedures of the NO adsorption tests and the DRIFTS study under actual conditions were similar with the ammonia adsorption tests except the atmosphere and temperature applied.

To comprehend the DRIFTS of the surface adsorbed NH_3, the NH_3-TPD (temperature programmed desorption) spectra were also obtained by monitoring the desorbed NH_3 when increasing the sample temperature at 5 °C/min in a 230 mL/min Ar flow, after NH_3 adsorbed at room temperature for 1 h. The masses of CaO and sulfated CaO were both 0.5 g. The outlet gas was analyzed during the heating process by a process mass spectrometer (AMETEK).

3. Results

3.1. NH₃-TPD on Fresh CaO and Sulfated CaO. Figure 2 shows the NH_3-TPD curves of analytical grade CaO and the sulfated CaO with 36.5% conversion with the particle diameter of 0.30–0.35 mm. The NH_3-TPD curve of analytical grade CaO indicates that there are two kinds of NH_3 desorption peaks: one near 350 °C, and the other near 550 °C. The relative peak positions of sulfated CaO change to the region of 550 to 650 °C. The increasing of NH_3 desorption temperature means increasing of adsorption strength, and therefore increasing of surface acidity strength. The decrease of NH_3 desorption peak is related to the pore plugging and surface area loss in CaO sulfation, which results in less NH_3 adsorption.
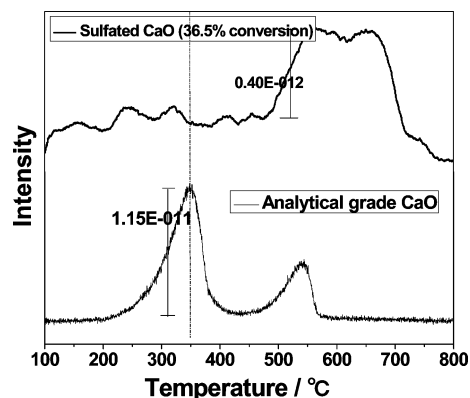

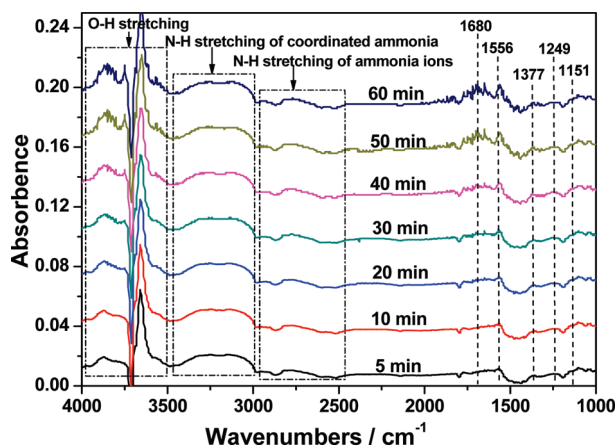**FIGURE 2. NH₃-TPD on the fresh CaO and sulfated CaO.**

FIGURE 3. DRIFTS of the adsorbed species arising from NH₃ (500 ppm NH₃) adsorption over CaO at 100 °C.

3.2. Activation of Ammonia over Analytical Grade CaO. Figure 3 shows the surface NH_3 adsorption of analytical grade CaO at 100 °C after it had been exposed to 500 ppm NH_3/N_2 for different periods. The results indicated that the adsorption over CaO was prompt. The bands around 3700 cm^{-1} (in the range of 3500–4000 cm^{-1}) could be assigned to O–H stretching (19). The bands at 3130 and 3270 cm^{-1} (in the range of 3100–3500 cm^{-1}) represent the N–H stretching of coordinated ammonia; the bands at 2780 and 2936 cm^{-1} (between 2500 and 3000 cm^{-1}) represent the N–H stretching of ammonia ions, and the peak at 1377 cm^{-1} represents the –NH₂ vibration (20, 21). The bands at 1151, 1249, and 1556 cm^{-1} represent the adsorbed NH_3 over Lewis acid sites, while the band at 1680 cm^{-1} indicates the NH_4^+ over Brönsted acid sites (22). The relative peak values indicate that NH_3 adsorption over CaO mainly exists in its coordinated form over Lewis acid sites, and the vibration of the adsorbed NH_3 is mainly in the form of –NH, whereas –NH₂ vibration is relatively low. Figure 4 shows the desorption of adsorbed NH_3 at 100 °C over CaO surface with changing temperature. When temperature increased from 100 to 400 °C, the vibration of N–H band between 2500 and 3500 cm^{-1} and the vibration of O–H band between 3500 and 4000 cm^{-1} disappeared quickly, together with the adsorption bands at 1151 and 1249 cm^{-1}, while the other bands remained almost unchanged. Between 400 and 600 °C, the adsorption peaks at 1680 and 1556 cm^{-1} disappeared. The DRIFTS results of the desorption of the adsorbed NH_3 over CaO surface agree with the NH_3-TPD curves in Figure 2, which suggests that there are two kinds of NH_3 desorption peaks over CaO, near 350 °C and near 550 °C, respectively.

3.3. Activation of Ammonia over Sulfated CaO. Figure 5 shows the surface NH_3 adsorption over sulfated CaO at 100 °C after being exposed to 500 ppm NH_3/N_2 for different times.
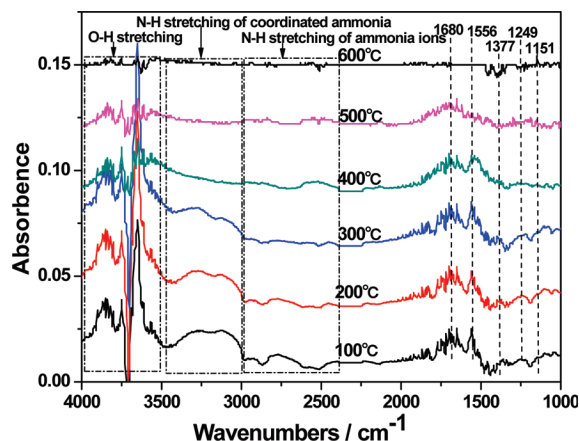
FIGURE 4. DRIFTS of CaO after 500 ppm NH$_3$ adsorption treated with N$_2$ at different temperatures.

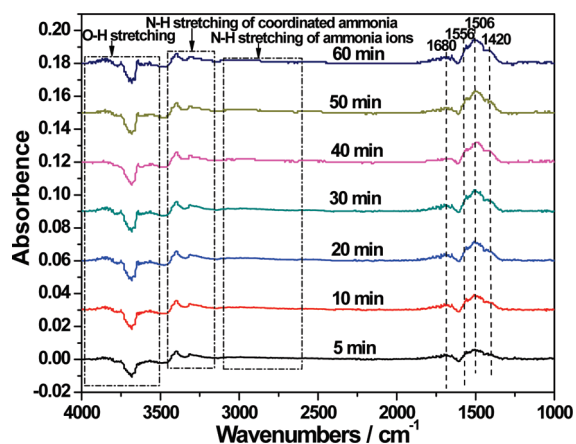**FIGURE 5. DRIFTS of the adsorbed species arising from NH$_3$ (500 ppm NH$_3$) adsorption over sulfated CaO at 100 °C.**

The bands in the range of 3500−4000 cm^{-1} could also be assigned to O−H stretching (*19*). The bands at 3310 and 3396 cm^{-1} (between 3100 and 3500) represent the N−H stretching of coordinated ammonia; the bands at 2600, 2790, 2955, and 3068 cm^{-1} (between 2500 and 3000 cm^{-1}) represent the N−H stretching of ammonia ions, while the peak at 1506 cm^{-1} represents the −NH$_2$ vibration (*20, 21*). The peak at 1556 cm^{-1} indicates the adsorbed NH$_3$ over Lewis acid sites, while the peak at 1420 and 1680 cm^{-1} indicates the NH$_4^+$ over Brönsted acid sites (*22−24*). The peak of NH$_3$ adsorbed on the Lewis acid sites was comparative to that adsorbed on the Brönsted acid sites. Comparing the vibration of adsorbed NH$_3$ over sulfated CaO, the −NH$_2$ vibration seems to be dominating, while the −NH vibration is relatively low. Figure 6 shows the desorption of the adsorbed NH$_3$ at 100 °C over sulfated CaO changing with the temperature. When the temperature increased from 100 to 400 °C, the peak of N−H vibration and O−H vibration disappeared, while the other peaks remained almost unchanged. When the temperature increased from 400 to 500 °C, all the vibration peaks at 1420, 1506, and 1556 cm^{-1} decreased simultaneously. When temperature increased to 600 °C, all of the adsorbed peaks disappeared. The DRIFTS results of the desorption of the adsorbed NH$_3$ over sulfated CaO also agree well with the NH$_3$-TPD curves of sulfated CaO in Figure 2, the desorption mainly exists at temperature higher than 500 °C.

3.4. DRIFTS of Sulfated CaO at Different Atmospheres. The NO adsorption and the SCR reaction over sulfated CaO have been investigated to further understand the SCR reaction mechanism over it. Previous studies have indicated that the byproduct of NO$_2$ is negligible during SCR reaction (*4*),
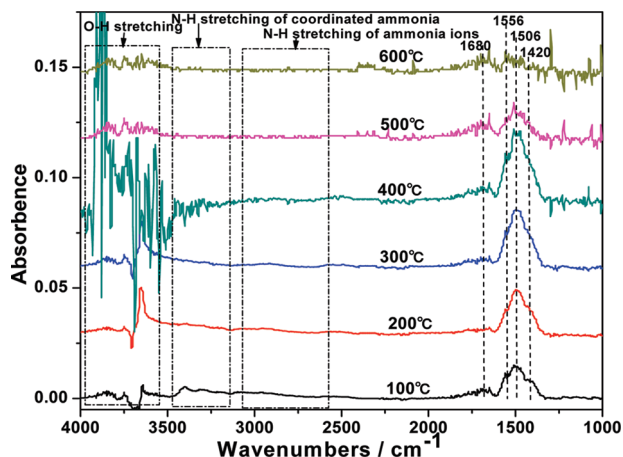

FIGURE 6. DRIFTS of sulfated CaO after 500 ppm NH$_3$ adsorption treated with N$_2$ at different temperatures.

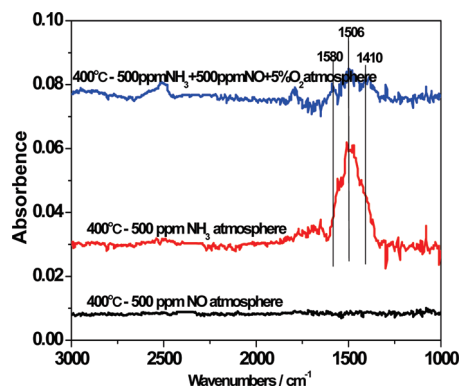**FIGURE 7. DRIFTS of sulfated CaO at different atmospheres.**

suggesting that there is virtually no reaction between NO and O$_2$. Therefore, DRIFTS experiments of NO + O$_2$ adsorption will not be conducted. Figure 7 shows the DRIFTS of sulfated CaO at 400 °C in the atmosphere of 500 ppm NO + N$_2$, 500 ppm NH$_3$ + N$_2$, and 500 ppm NH$_3$ + 500 ppm NO + 5% O$_2$ + N$_2$. The temperature of 400 °C was chosen because the reaction intermediates could be seen more clearly under this temperature as the reaction was not too fast. The results of NO adsorption indicated that, at 400 °C, no NO was adsorbed over sulfated CaO, while the NH$_3$ adsorption at 400 °C showed the bands near 1580, 1506, and 1410 cm^{-1}. The DRIFTS of sulfated CaO in NH$_3$ + NO + O$_2$ + N$_2$ also showed the peaks near 1580, 1506, and 1410 cm^{-1}. The bands near 1580 cm^{-1} indicate NH$_3$ adsorbed over Lewis acid sites, while the bands near 1410 cm^{-1} indicate NH$_3$ adsorbed over Brönsted acid sites, and the bands near 1506 cm^{-1} indicate the NH$_2$ stretching. The bands of sulfated CaO in NH$_3$ were similar to the bands of sulfated CaO under SCR reaction conditions, which once again indicated that NH$_3$ adsorbed first over sulfated CaO and then reacted with NO during the SCR process.
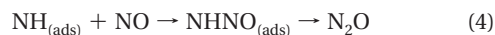
4. Discussion

The DRIFTS of NH$_3$ and NO adsorption over sulfated CaO have suggested that NH$_3$ is more easily adsorbed than NO. Hence, the catalytic mechanism should be associated with adsorbed NH$_3$ reacting with gaseous NO. The DRIFTS of ammonia adsorption over catalysts in Figures 3 and 5 indicate that both Lewis and Brönsted acid sites are present on the surface, which is in accordance with previous research (*25*). Over CaO, NH$_3$ adsorbed on Lewis acid sites is dominating. Over sulfated CaO, however, NH$_3$ adsorbed on Brönsted acid sites becomes relatively more dominant than that over CaO.

(a) H-bonded NH_3 on oxidate sites (b) Lewis-bonded NH_3 (C) ammonia ions bonded at Brønsted acid sites
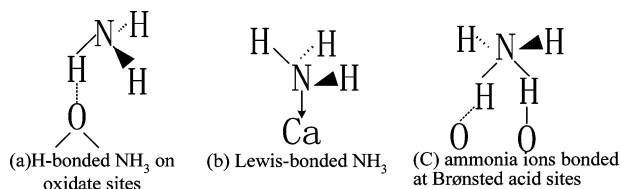
FIGURE 8. Proposed structures for ammonia adsorbed on CaO.

Previous studies have found that strong Brönsted acidity formed during sulfation process (*26, 27*). Nevertheless, it is ammonia adsorbed over acid sites, though the overall catalytic effects over CaO and sulfated CaO are very different, and this may be due to the different intermediates produced from adsorbed NH_3. It has been revealed that the H-abstraction of adsorbed NH_3 over the catalyst is the key step to decide the direction of catalytic activity, and the H-abstraction intermediates from adsorbed NH_3 could be NH_2 or NH (*28, 29*): If the H-abstraction intermediate is NH, it could react as routes 4 or 5:

$$NH_{(ads)} + NO \rightarrow NHNO_{(ads)} \rightarrow N_2O \quad (4)$$

$$NH_{(ads)} + O_{(lattice)} \rightarrow HNO \rightarrow NO \quad (5)$$

If the H-abstraction intermediate is NH_2, it could react as routes 6 or 7:

$$NH_{2(ads)} + NO \rightarrow NH_2NO_{(ads)} \rightarrow N_2 \quad (6)$$

$$NH_{2(ads)} \rightarrow N_2H_4 \rightarrow N_2 \quad (7)$$
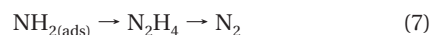
The reactions 4−7 indicate that the intermediates of NH and NH_2 actually determine the selectivity of NH_3. The DRIFTS of NH_3 adsorption indicate more NH over CaO and more NH_2 over sulfated CaO. Therefore, it is reasonable to believe that the H-abstraction intermediate over CaO was mainly NH, and the H-abstraction intermediate over sulfated CaO was mainly NH_2. It is apparent that CaO demonstrates catalytic effect on NH_3 oxidation to NO, and sulfated CaO is selective for NO reduction by NH_3. Thus, it could be concluded that the H-abstraction degree of the adsorbed ammonia is the key step to deciding the catalyst activity no matter ammonia is being adsorbed over what acid sites.

Combining the DRIFTS results with CaO catalytic activity for NH_3 oxidation, the adsorbed NH_3 over CaO could be described as in Figure 8. The proposed structures includes (a) H-bonded NH_3 on oxygen sites, (b) Lewis-bonded NH_3, and (c) ammonia ions bonded at Brönsted acid sites. The DRIFTS results in Figure 3 indicated that Lewis acid sites were more than Brönsted acid sites over CaO, i.e., structures (a) and (b) were much more prevalent than structure (c). In structures (a) and (b), two H atoms of adsorbed NH_3 are apt to combine with O to form H_2O, while the produced NH follows route 4 or 5. Previous studies of NH_3 oxidation over CaO have indicated that −CaN would be formed after NH_3 adsorbed on the CaO surface, and then the formed −CaN would react with O_2 to reproduce CaO and NO, or would react with NO to produce N_2O (*6*). Considering almost no N_2O has been found during the oxidation of NH_3 over CaO in the stream of $NH_3 + NO + O_2 + N_2$ (*6, 30*), −CaN reacting with NO is of minor importance, suggesting that reaction 4 is of minor importance under this condition. Therefore, the main reaction is −CaN reacting with O_2 to form CaO and NO and providing surface O to reaction 5. Hence, it could be concluded that the structures (a) and (b) in Figure 8 were the main structures for ammonia adsorbed over CaO producing NH and reacting with surface oxygen to produce NO.

The DRIFTS of ammonia adsorption over sulfated CaO in Figure 5 indicated that the ammonia adsorbed by Brönsted

(i) Lewis-bonded NH_3 (ii) ammonia ions bonded at Brønsted acid sites
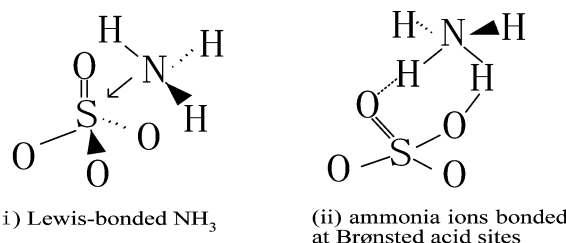
FIGURE 9. Proposed structures for ammonia adsorbed on sulfated CaO.

acid sites was comparative to that by Lewis acid sites. The NH_2 stretching band was significantly more intensive than the NH stretching bands. Furthermore, the TPD results in Figure 2 indicated that the NH_3 desorption temperature increased as CaO sulfated and surface acidity strength increased. Previous studies have already indicated the coordinated modes of SO_4^{2-} (*5*). Hence, combined with the DRIFTS results, the catalytic activity of sulfated CaO for SCR reaction, and SO_4^{2-} structure, the NH_3 adsorption forms over sulfated CaO could be described by Figure 9. The proposed structures includes (i) Lewis-bonded NH_3; and (ii) ammonia ions bonded at Brönsted acid sites. As SO_4^{2-} increases the catalyst acidity strength, the H-abstraction of adsorbed NH_3 by surface oxygen over SO_4^{2-} is not as easy to be abstracted over CaO. Hence, over sulfated CaO, the H-abstraction of adsorbed ammonia is mainly NH_2. For structure (ii) in Figure 9, the adsorbed ammonia over Brönsted acid sites could be easily activated in amide NH_2 species, and then reacts with gas-phase NO to produce N_2 and H_2O. Accordingly, in structure (i), the ammonia adsorbed over Lewis acid sites could also be activated to amide NH_2 species by the following step 8, and this mechanism is similar to that proposed by Ramis et al. over vanadium oxide catalysts (*31*):

$$NH_3 + S^{n+} + O = \rightarrow S^{(n-1)} - NH_2 + OH \quad (8)$$
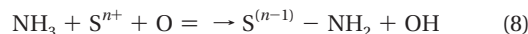
The amide NH_2 formed from the electron excursion of S agrees with the DRIFTS results over sulfated CaO that NH_2 stretching dominates no matter whether the NH_3 is adsorbed over Lewis or Brönsted acid sites.

Also, from the perspective of binding energy, the Ca−O ionic bond is weaker than the S=O covalent band in SO_4^{2-}. It has been suggested that, due to the strong binding of lattice oxygen, the NH_3 oxidation rate should be fairly low (*32, 33*). Hence, the H-abstraction of adsorbed ammonia over CaO was further than that over sulfated CaO, for the lattice oxygen in CaO was more active than that of SO_4^{2-}, which means that the H-abstraction degree is affected by the oxidation ability of the catalyst.

Therefore, the reaction mechanisms of NH_3 oxidation over CaO and the NO reduction by NH_3 over sulfated CaO have been understand by these DRIFTS experiments, which is very useful to get full use of the catalyst activity in the simultaneous removal of SO_2 and NO_x.

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