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Al_2O_3-coated cordierite honeycomb supported CuO catalyst for selective catalytic reduction of NO by NH_3: Surface properties and reaction mechanism

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ABSTRACT

Al_2O_3-coated cordierite supported CuO catalyst shows high activities for selective catalytic reduction (SCR) of NO by NH_3 at 350–500 °C after being sulfated by SO_2. Its surface properties and reaction mechanism are elucidated in this paper by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) coupled with mass spectroscopy. Results show that the catalyst has both Lewis and Brønsted acid sites, the Brønsted acidity is far weaker than the Lewis acidity and the protonated ammonia on Brønsted sites is less stable than the coordinated ammonia on Lewis sites. Ammonia coordinated on sulfated $CuAl_2O_4$ may transfer to NH_2–NH_2, where aluminum species is responsible for NH_3 storage and copper species is responsible for activation of NH_3 to NH_2. The SCR reaction involves the adsorbed NH_2–NH_2 and gaseous NO, following Eley–Rideal mechanism. When NH_3 is insufficient, NO may convert to NO_2 through oxidation by O_2 or to N_2O and NO_2 through disproportionation.

1. Introduction

Selective catalytic reduction (SCR) of NO by NH_3 in the presence of oxygen is a well-proven reaction for NO removal from flue gases of stationary sources [1,2]. V_2O_5/TiO_2 based catalysts have been widely used for this reaction in practice [1,3] and a variety of other catalysts are being developed. Recently, we found that CuO supported on an Al_2O_3-coated cordierite monolith (CuO/cordierite-Al_2O_3) is quite active for the SCR especially after being sulfated by SO_2 [4–6]. Therein, the Al_2O_3 coating was synthesized from $Al(NO_3)_3$ and urea, which is in gamma form, homogeneous and physically stable [5,6]. The catalyst is promising for application because it combines the high activity of CuO/Al_2O_3 and the high mechanical strength and low flow resistance of the cordierite honeycomb. However, up to date limited knowledge is available on the catalyst's surface properties and the SCR mechanism.

CuO/Al_2O_3, the main active component of CuO/cordierite-Al_2O_3 catalyst, has been studied in the past. Centi et al. [7–9] reported that the SCR proceeded via oxidation of NO and ammonium nitrate is the intermediate. However, they also proposed that the SCR proceeded via splitting of NH_3 on Cu^{2+} [8]. Pradier [10] studied NH_3 adsorption on pure CuO and found that CuO lacks Brønsted acidity. While these reports are very useful for understanding of CuO/cordierite-Al_2O_3 catalyst, further studies are still needed because interactions between the catalyst's components may have significant effect.

In view of this situation, a series of experiments were carried out in this work through a combined in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and mass spectroscopy (MS) to understand the catalyst's surface acid sites, the nature of catalytic sites and the SCR mechanism. The knowledge obtained may also be useful for improvement in catalytic activity and selectivity of CuO/Al_2O_3 based catalyst.

2. Experimental

2.1. Catalyst preparation

The cordierite honeycomb used in this work is a commercial product (Jingtu Ltd., Taiyuan, China) with a cell density of 200 cells per square inch. γ-Al_2O_3 was coated on the monolith via impregnation with an alumina sol synthesized from $Al(NO_3)_3$ and urea, followed by drying at 110 °C and calcining at 500 °C. Weight measurement showed that the amount of Al_2O_3 coated on the monolith was about 3.2 wt%. CuO was supported on the Al_2O_3-coated cordierite by dip-impregnating with a $Cu(NO_3)_2$ solution, followed by drying at 110 °C and calcining at 500 °C. The Cu loading determined by inductively coupled plasma (ICP) was 1.16 wt%. The sample was then exposed to a gas stream containing SO_2, O_2, H_2O and Ar at 400 °C for sulfation. The final sample was marked as CuO/cordierite-Al_2O_3(S). For comparison, other two samples were prepared, namely Al_2O_3/cordierite(S) (Al_2O_3-coated cordierite

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sulfated in $SO_2 + O_2 + H_2O$ at 400 °C) and CuO/cordierite(S) (CuO-supported cordierite sulfated in $SO_2 + O_2 + H_2O$ at 400 °C).

2.2. XPS characterization

X-ray photoelectron spectroscopy (XPS) was carried out at room temperature on a VG Scientific ESCA-Lab 220I-XL spectrometer with A1 Kα radiation in twin anode ($h\nu = 1486.6$ eV) at 10 kV × 20 mA. The binding energies were calculated with respect to the C 1s peak at 284.6 eV. Data analysis was performed with the XPS-Peak3.1 program and the spectra were fitted with an optimal Gaussian–Lorentzian ratio after subtraction of a Shirley-type baseline.

2.3. Activity test

SCR activity of the catalyst was measured in a fixed-bed tubular reactor. A monolithic catalyst sample ($\Phi 20 \times 30$ mm) was fitted in the reactor and heated to a desired temperature under a flow of Ar. At steady state, a gas mixture containing 500 ppm NO, 5.5% O_2, 2.5% H_2O, 500 ppm NH_3 and balance Ar was introduced to the reactor at a flow rate of 440 ml/min, corresponding to a superficial space velocity of 2800 h^{-1}. The concentrations of NO and O_2 in the inlet and outlet of the reactor were simultaneously measured on-line by a Flue Gas Analyzer (KM9106, Quintox, Kane).

2.4. DRIFTS-MS experiments

DRIFTS experiments were performed on a temperature-controlled diffuse reflectance cell (ZnSe windows, Spectra-Tech 0030-102) coupled to an infrared spectrometer (Equinox55 Bruker) with KBr optics. Spectra in reflection mode were recorded by accumulating 64 scans at a resolution of 4 cm^{-1} using a MCT detector. First of all, an Al mirror was mounted on the ceramic frit (Al_2O_3) inside the cell and a single-beam background was collected. Based on this background, a series of reflection spectra were recorded. Reflection spectra of a sample free of adsorbate are termed $R_{\text{cat-}T}$ (the suffix 'T' denotes the collection temperature) and reflection spectra of the sample adsorbed with adsorbates were termed $R_{\text{cat-ads-}T}$ ("ads" denotes the kind of adsorbate). In some cases, reflection spectra are collected in the presence of gaseous adsorbates, which are termed $R_{\text{cat+ads-}T}$ to differentiate from $R_{\text{cat-ads-}T}$.

The DRIFTS spectra presented in this paper are all in Kubelka–Munk unit, which are obtained through Formula (1), where relative reflectance R' is defined in Formula (2) to eliminate interference of the supports. Detailed information on the spectrum transformation can be seen in the literature reported by Sirita et al. [11].

$$KM = \frac{(1-R')^2}{2R'} \tag{1}$$

$$R' = \frac{R}{R_{\text{cat-}T}} \quad (R = R_{\text{cat-ads-}T} \text{ or } R_{\text{cat+ads-}T}) \tag{2}$$

2.4.1. NO adsorption behavior

After a single-beam background was collected as described above, a ground catalyst sample with particle sizes smaller than 120 mesh was loaded into the ceramic frit without packing or dilution. The sample was pretreated in situ under a flow of Ar (50 ml/min) at 400 °C for 1 h to remove impurities from the surface. A reflection spectrum was then recorded at 400 °C and termed $R_{\text{cat-400}}$. Finally, a NO/Ar flow (3600 ppm NO) was introduced into the cell and a reflection spectrum was recorded at 20 min, which is termed $R_{\text{cat+NO-400}}$. Kubelka–Munk spectrum is obtained through Formula (1) to investigate NO adsorption behavior.

2.4.2. Determination of surface acidity

After being pretreated at 400 °C as described above, the catalyst sample was cooled down from 400 to 40 °C at a rate of 10 °C/min. In this period, a series of reflection spectra were collected at a 20 °C interval and termed $R_{\text{cat-}T}$. An NH_3/Ar flow (3600 ppm NH_3) was introduced at 40 °C for 2 h for in situ NH_3 adsorption. Then, the sample was purged with Ar until no NH_3 was detected in the effluent. Finally, temperature-programmed desorption (TPD) was performed under the Ar flow at a heating rate of 10 °C/min, and a series of reflection spectra were collected at a 20 °C interval from 40 to 400 °C. These spectra are termed $R_{\text{cat-NH}_3\text{-}T}$. A series of Kubelka–Munk spectra at different temperatures were obtained through Formula (1).

2.4.3. SCR mechanism study

After the TPD experiment, the catalyst sample was oxidized in situ under an O_2/Ar flow (3.2% O_2) at 400 °C and then re-exposed to the NH_3/Ar flow. A reflection spectrum was collected after 20 min and termed $R_{\text{cat+NH}_3\text{-400}}$. It should be noted that the "+" signal in the subscript of $R_{\text{cat+NH}_3\text{-400}}$ denotes "in a flow containing NH_3" while the "-" signal in the subscript of $R_{\text{cat-NH}_3\text{-400}}$ showed "pre-adsorbed with NH_3". NO + O_2 was then added to the feed and a reflection spectrum was collected at 5 min and termed $R_{\text{cat+NH}_3\text{+NO-400}}$. Finally, NH_3 was removed from the feed and NO and O_2 were remained. Two reflection spectra were collected at 5 and 25 min and termed $R_{\text{cat-NH}_3\text{+NO-400(5)}}$ and $R_{\text{cat-NH}_3\text{+NO-400(25)}}$, respectively. All the reflection spectra obtained were presented in Kubelka–Munk form as defined by Formula (1).

In all the cases, the effluent gas of the DRIFTS spectrometer was monitored on-line by a mass-quadrupole detector (Balzers, OmniStar 200).

3. Results and discussion

3.1. Adsorption and activation of NH_3 over CuO/cordierite-Al_2O_3(S)

Fig. 1 shows DRIFTS spectra of CuO/cordierite-Al_2O_3(S) pre-adsorbed with NH_3 during TPD. It should be noted that the peaks in the spectra are mainly from the adsorbed species because the influence of the support has been eliminated by using the relative reflectance R' in the Kubelka–Munk calculation. As can be seen, the spectra present almost indiscernible NH deformation peaks at 1800–1100 cm^{-1}, suggesting that the amount of ammonia adsorbed on CuO/cordierite-Al_2O_3(S) is very little and the acid sites are weak according to the literatures [12,13].

The spectra present obvious NH stretching peaks at 3500–2500 cm^{-1}. Specifically, the spectrum at 40 °C shows three sharp peaks at 3336, 3243 and 3181 cm^{-1}, a broad peak at 3270–3205 cm^{-1}, a weak peak at 3053 cm^{-1} and a shoulder peak at 2868 cm^{-1}. With increases in temperature, following phenomena are observed: (1) a new strong peak appears at 3274 cm^{-1} and the peak at 3181 cm^{-1} shifts to 3190 cm^{-1} when the temperature is increased to 160 °C; (2) the peaks at 3053, 2868 cm^{-1} and 3243 cm^{-1} disappear when temperature is increased to 320 °C, but other peaks at 3336, 3274 and 3190 cm^{-1} are still visible; (3) the peaks at 3336 and 3190 cm^{-1} almost disappear when temperature is increased to 400 °C, but the peak at 3274 cm^{-1} is still discernible. According to IR results of NH_3 adsorptions on CuO/TiO_2 [14] and V_2O_5/TiO_2 [15,16], the peaks at 3336, 3243 and 3181 cm^{-1} can be assigned to NH stretching of NH_3 coordinated on Lewis acid sites (ν_{NH} of NH_3), and the peaks at 3053 and 2868 cm^{-1} can be assigned to NH stretching of NH_4^+ adsorbed on Brønsted acid sites (ν_{NH} of NH_4^+). Clearly, both Lewis and Brønsted acid sites present

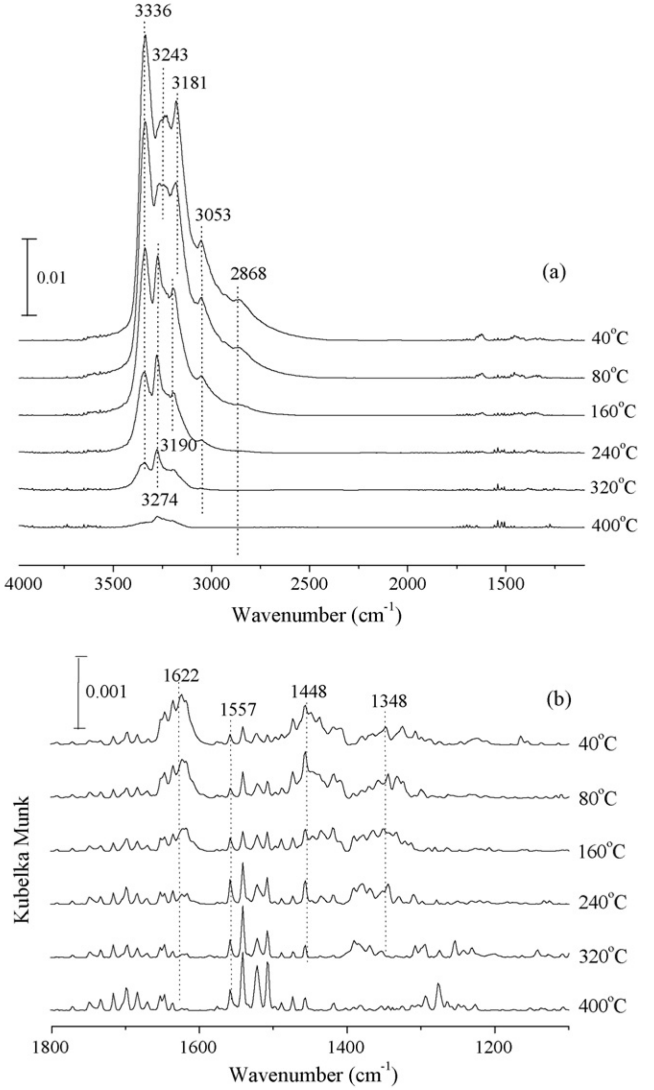

Fig. 1. DRIFTS spectra in Kubelka–Munk unit of CuO/cordierite-Al_2O_3(S) pre-adsorbed with NH_3 during TPD: (a) region of 4000–1100 cm^{-1}; (b) magnified region of 1800–1100 cm^{-1}. The sample was firstly treated in Ar at 400 °C for 1 h and then cooled down. The reflection spectra collected during cooling are used as the reference spectra.

on CuO/cordierite-Al_2O_3(S) and there are various types of Lewis acid sites. In addition, acidities of the Lewis sites are relatively stronger than those of the Brønsted sites and NH_3 coordinated on the Lewis sites is thermally more stable than NH_4^+ adsorbed on the Brønsted sites. The peak at 3274 cm^{-1} indicates the presence of a stable species other than NH_3 since its behavior during heating is different from other peaks, which will be discussed later.

In the magnified NH deformation region of 1800–1100 cm^{-1} (Fig. 1(b)), asymmetrical deformation peaks can be found at 1622 cm^{-1} (δas of NH in NH_3) and 1448 cm^{-1} (δas of NH in NH_4^+). These two peaks fade with increasing temperature due to desorption of NH_3 and NH_4^+. The peak at ~1560 cm^{-1} (assigned to NH_2 scissoring) is generally regarded as a characteristic of NH_2–NH_2 [14,17,18] and that at 1348 cm^{-1} is assigned to NH_2 wagging of N_2H_4 (hydrazine) [14,17]. Since the change trend of the peak at 3274 cm^{-1} is similar to those at ~1560 and 1348 cm^{-1}, it can also be assigned to NH_2–NH_2.

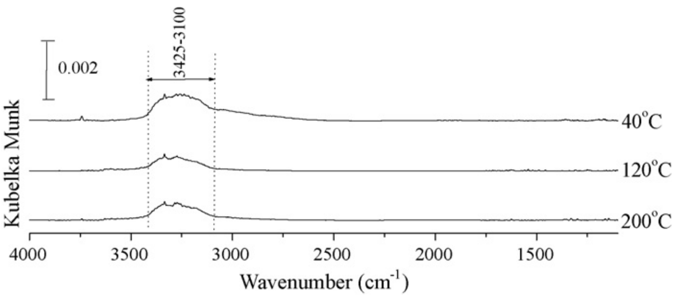

Fig. 2. DRIFTS spectra in Kubelka–Munk unit of the cordierite pre-adsorbed with NH_3 during TPD. The reference spectra are collected on the cordierite as described for CuO/cordierite-Al_2O_3(S).

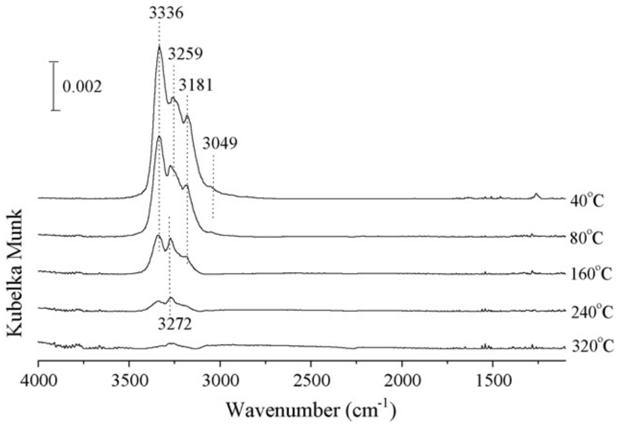

Fig. 3. DRIFTS spectra in Kubelka–Munk unit of CuO/cordierite(S) pre-adsorbed with NH_3 during TPD. The reference spectra are collected on CuO/cordierite(S) as described for CuO/cordierite-Al_2O_3(S).

3.2. The acid sites on CuO/cordierite-Al_2O_3(S)

To elucidate the acid sites on CuO/cordierite-Al_2O_3(S), three samples, Al_2O_3/cordierite(S) (without CuO), CuO/cordierite(S) (without Al_2O_3) and the cordierite were also subjected to NH_3 adsorption and TPD. Kubelka–Munk spectra of these samples shown in Figs. 2–4 indicate an intensity order of Al_2O_3/cordierite(S) > CuO/cordierite(S) ≫ cordierite. Furthermore,

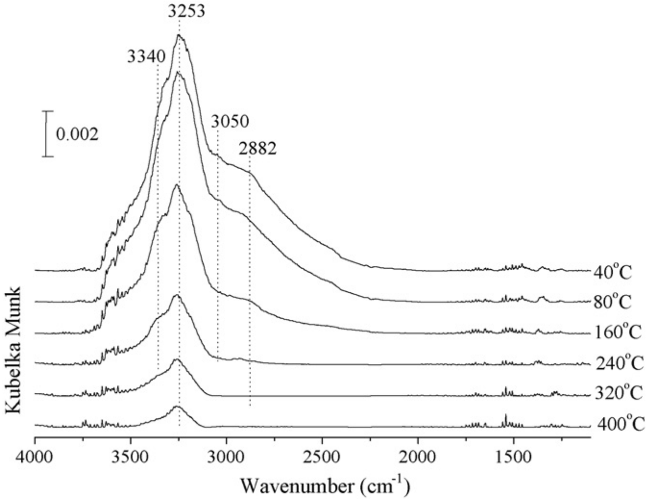

Fig. 4. DRIFTS spectra in Kubelka–Munk unit of Al_2O_3/cordierite(S) pre-adsorbed with NH_3 during TPD. The reference spectra are collected on Al_2O_3/cordierite(S) as described for CuO/cordierite-Al_2O_3(S).

Table 1
Wavenumber and assignment of DRIFTS bands of the adsorbed species.

Wavenumber/cm^{-1}	Assignment	Adsorption sites
3340 ± 5	Coordinated NH_3	Cu, Al
3278 ± 5	Coordinated NH_2	Cu
3270–3205	Coordinated NH_3	Cu, Al
3185 ± 5	Coordinated NH_3	Cu
3049 ± 5	Protonated NH_3	Cordierite, Al
2868	Protonated NH_3	Al

Table 2
Binding energy values (in eV) of the fresh and sulfated CuO/cordierite-Al_2O_3.

Catalyst	Cu $2p_{3/2}$	Al 2p	S 2p
Fresh CuO/cordierite-Al_2O_3	933.8 − 935.4	73.9	
Sulfated CuO/cordierite-Al_2O_3	935.6 937.5	74.2	168.7 169.8

it seems that the sum of the spectra intensity of CuO/cordierite(S) (0.007, Fig. 3) and Al_2O_3/cordierite(S) (0.012, Fig. 4) is far smaller than that of CuO/cordierite-Al_2O_3(S) (0.035, Fig. 1), suggesting strong interactions between CuO and Al_2O_3 in CuO/cordierite-Al_2O_3(S).

The cordierite presents both Lewis and Brønsted acid sites of weak acidity as indicated in Fig. 2 by the weak broad peaks at 3425–3100 (ν_{NH} of NH_3) and at 3049 cm^{-1} (ν_{NH} of NH_4^+). Supporting CuO onto the cordierite leads to significant increases in the peaks at 3336, 3259 and 3181 cm^{-1} (Lewis acid sites) but little change in the peak at 3049 cm^{-1} (Brønsted acid site), as shown by the spectrum at 40 °C in Fig. 3. This indicates that Brønsted acid site on CuO/cordierite(S) is from the cordierite but not from CuO and $CuSO_4$, which agrees with the report that CuO and $CuSO_4$ lack Brønsted acidity [10,17]. The disappearances of the peak at 3049 cm^{-1} at 80 °C and the peaks at 3336 and 3181 cm^{-1} at 320 °C, and the formation of the new peak at 3272 cm^{-1} (ν_{NH} of NH_2–NH_2) at 160 °C are all similar to those discussed earlier for CuO/cordierite-Al_2O_3(S).

Supporting Al_2O_3 on cordierite also leads to increases in Lewis acid sites as indicated by the shoulder peak at 3340 cm^{-1} and the sharp peak at 3253 cm^{-1} at 40 °C (Fig. 4). The shoulder peak at 3050–2800 cm^{-1} at 40 °C indicates presence of Brønsted acid sites on both cordierite (3050 cm^{-1}) and Al_2O_3 (2882 cm^{-1}) [14]. The only retaining of the peak at 3253 cm^{-1} at 320 °C and higher indicate that NH_4^+ on the Brønsted acid sites is thermally less stable than NH_3 on the Lewis acid sites, which is similar to that discussed earlier for CuO/cordierite-Al_2O_3(S).

The DRIFTS spectra presented in Figs. 1–4 clearly show that for CuO/cordierite-Al_2O_3(S) catalyst, the Brønsted acid sites are from the aluminum species and the cordierite while the Lewis acid sites are relatively complex. The peak at 3336 cm^{-1} is due to NH_3 coordinated on copper and aluminum species, the peak at ~3181 cm^{-1} is due to NH_3 coordinated on copper species and the peak at 3274 cm^{-1} is due to NH_2–NH_2 coordinated on copper species. For clarity, Table 1 summarizes assignment of the observed peaks and adsorption sites.

NH_2–NH_2 species should be noted because it disappears at 320 °C over CuO/cordierite(S) but is visible at 400 °C over CuO/cordierite-Al_2O_3(S). This suggests that the formation of NH_2–NH_2 species on CuO/cordierite-Al_2O_3(S) is related to other species besides copper. It is likely the aluminum species since the coordinated NH_3 on Al_2O_3/cordierite(S) is stable. That is to say, the aluminum species plays a role in storing NH_3 and the copper species plays a role in activating dehydrogenation of NH_3 to NH_2.

The roles of copper and aluminum species in the formation of NH_2–NH_2 may suggest presence of the $CuAl_2O_4$ phase in CuO/cordierite-Al_2O_3(S). Strohmeier et al. [19] and Friedman et al. [20] reported that there are three types of copper species in CuO/Al_2O_3: CuO, spinel-like $CuAl_2O_4$ formed at low CuO loadings and low calcination temperatures (around 500 °C), and bulk-like $CuAl_2O_4$ formed at high calcination temperatures (900 °C or higher). If this is applicable to CuO/cordierite-Al_2O_3 studied in this work, CuO and spinel-like $CuAl_2O_4$ should be the main forms of copper before sulfation. To verify this hypothesis, XPS was performed on the fresh and the sulfated CuO/cordierite-Al_2O_3 and the results are shown in Table 2 (obtained by the Gaussian–Lorentzian fit). The fresh catalyst shows two Cu $2p_{3/2}$ peaks at 933.8 and 935.4 eV. The former can be assigned to Cu^{2+} in CuO and the latter to Cu^{2+} in $CuAl_2O_4$ as did in the literatures [19,21,22]. The sulfated catalyst shows two Cu $2p_{3/2}$ peaks at 935.6 and 937.5 eV. The former can be assigned to $CuSO_4$ as did in the literatures [19,23], which is confirmed by the split satellite peaks at 940.8 and 943.9 eV in this work, the characteristic of Cu^{2+} in $CuSO_4$. The latter can be attributed to Cu^{2+} in sulfated $CuAl_2O_4$ since the electro-negativity of SO_4^{2-} is stronger than $Al_2O_4^{2-}$ [24], and the binding energy of Cu $2p_{3/2}$ of $CuAl_2O_4$ should shift to a higher degree after the sulfation process. The binding energies of S 2p indicate presence of another S^{6+} species (169.8 eV) in addition to S^{6+} in $CuSO_4$ (168.7 eV) in the sulfated catalyst, further suggesting the presence of sulfated $CuAl_2O_4$. It is very likely, therefore, that NH_2–NH_2 is formed on sulfated $CuAl_2O_4$.

3.3. Mechanism of the SCR reaction

3.3.1. MS results

Fig. 5 presents MS results of CuO/cordierite-Al_2O_3(S) obtained in a ten-step (A–J) transient experiment at 400 °C. For clarity, the signals of m/e = 17, 28, 30, 46, 44 are enlarged 20, 10, 100, 10,000 and 1000 times, respectively. The N_2 signal, m/e = 28, is mainly used to judge the occurrence of the SCR reaction.

Since TPD experiment presented in Section 3.1 was carried out before the transient experiment, the catalyst was subjected to in situ oxidization under an O_2/Ar flow first (Stage A). The increases in signals m/e = 28 (N_2) and 44 (N_2O) indicate presence of ammonia on the catalyst after the TPD. It should be noted that the amount of residual ammonia is very small because it is not detectible by DRIFTS as evidenced in Fig. 1 (spectrum at 400 °C).

Stages B–E are designed to investigate NH_3 behavior in the SCR reaction. Stage B starts with replacement of the O_2/Ar feed by NH_3/Ar. As a result, the signals m/e = 28 and 44 decrease to the base-

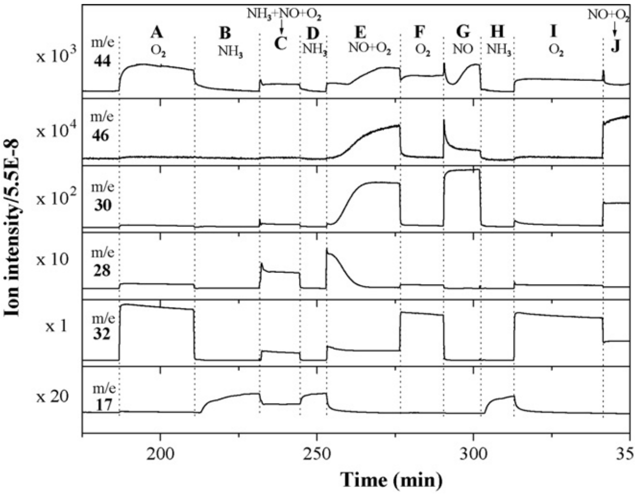

Fig. 5. MS results of transient response experiment over CuO/cordierite-Al_2O_3(S) at 400 °C.

line as expected. The introduction of NO + O_2 into the NH_3/Ar feed initiates Stage C, where limited increase in signal m/e = 30 (NO), significant decrease in signal m/e = 17 (NH_3) and increase in signal m/e = 28 (N_2) are observable. These observations indicate the occurrence of SCR reaction between NO, O_2 and NH_3. The slight increase in signal m/e = 44 (N_2O) suggests very limited side reaction at 400 °C. The removal of NO + O_2 from the feed in Stage D allows adsorption and accumulation of NH_3 on the surface. The replacement of the NH_3/Ar flow by NO + O_2/Ar flow initiates Stage E, where the behavior of signal m/e = 28, i.e. instantly increases to a high level followed by a gradual decrease to the baseline in 15 min, and its mirror pattern of signal m/e = 30 indicate occurrence of SCR reaction in the absence of gaseous NH_3. The instantaneous but small increase in signal m/e = 44 (N_2O) in the first 8 min in Stage E (NO + O_2) is very similar to that in Stage C (NH_3 + NO + O_2), suggesting limited side reaction of SCR. The significant increases in m/e = 44 and m/e = 46 after 8 min indicate substantive formation of N_2O and NO_2 when most of the adsorbed NH_3 is consumed. This behavior was possibly due to disproportionation of NO into NO_2 and N_2O, as reported by Suárez et al. [25]. It is also possible that the formation of N_2O is due to oxidation of the residual adsorbed-NH_3 by O_2 as observed in Stage A and the formation of NO_2 is due to oxidation of NO.

After the O_2 treatment of the catalyst in Stage F, a NO/Ar flow was introduced to start Stage G, where signals m/e = 44 (N_2O) and 46 (NO_2) follow a similar behavior in the first 5 min, i.e. instant increases to high levels and then gradual decreases. Subsequently, signal m/e = 44 starts to increase to a higher steady level while signal m/e = 46 keeps decreasing to a new steady level higher than the baseline. The relative intensities of m/e = 44 and 46 may suggest that reaction of NO with the residual O_2 and disproportionation of NO simultaneously occur in the initial while only disproportionation of NO remains in the subsequent. Comparing Stage E (NO + O_2) with Stage G (NO), it is clear that signal m/e = 46 (NO_2) in Stage E is stronger than that in Stage G, which confirms the reaction of NO and O_2 to form NO_2 in Stage E.

The replacement of NO/Ar flow by NH_3/Ar flow in Stage H leads to disappearance in signals of m/e = 30, 44 and 46, which indicate absence of the SCR reaction and thus the absence of NO on the catalyst. Stages I and J are designed to study the effect of O_2 on NO adsorption. Introduction of NO to the O_2/Ar flow (Stage I) in Stage J results in an instant increase in signal m/e = 46 (NO_2), suggesting oxidation of NO. This further indicates limited adsorption of NO on the catalyst in the presence of O_2.

The MS results presented above may indicate that (1) there are at least two types of adsorbed NH_3 over CuO/cordierite-Al_2O_3(S): reactable with NO + O_2 to form N_2 for the SCR and reactable with O_2 to form N_2O; (2) when NH_3 on the catalyst is insufficient for the SCR reaction, NO partially reacts with O_2 to form NO_2 and partially disproportionates into N_2O and NO_2.

3.3.2. *DRIFTS results*

To further understand the SCR reaction over the CuO/cordierite-Al_2O_3(S) catalyst, adsorption of NO and NH_3, as well as reaction of NO with adsorbed NH_3 were studied by DRIFTS at 400 °C. The Spectrum (a) in Fig. 6 is for NO adsorption obtained through Formula (1) with $R' = (R_{\text{cat+NO-400}}/R_{\text{cat-400}})$. The absence of any peak in the spectrum confirms that NO cannot adsorb on the catalyst surface at 400 °C. The Spectrum (b) is for NH_3 adsorption where $R' = (R_{\text{cat+NH}_3\text{-400}}/R_{\text{cat-400}})$. The intensive peaks, including NH stretching in NH_3 coordinated on Lewis acid sites (3341, 3282 and 3188 cm^{-1}) and NH stretching in NH_4^+ adsorbed on Brønsted acid sites (3049 and 2858 cm^{-1}), indicate strong NH_3 adsorption on the catalyst. The Spectrum (c) is obtained after exposure of the NH_3-adsorbed catalyst in a NO/Ar flow for 10 min, based on Formula (1) with $R' = (R_{\text{cat-NH}_3\text{+NO-400}}/R_{\text{cat+NH}_3\text{-400}})$. The absence of any peak confirms again the inability of the catalyst to adsorb NO. These results indicate that the SCR reaction over the catalyst follows the Eley–Rideal mechanism that involves a reaction between adsorbed NH_3 and gas phase NO. This conclusion is different from that of Centi et al. [7,8] for a CuO/Al_2O_3 catalyst, in which Cu^{2+}–NO_2 and Cu^{2+}–N_2O_3 were identified as the intermediates.

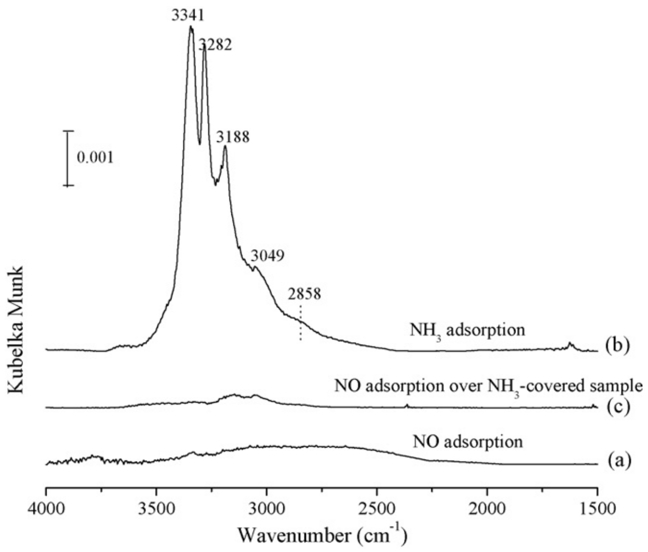

Fig. 6. DRIFTS spectra in Kubelka–Munk units of CuO/cordierite-Al_2O_3(S) exposed to NO or NH_3 at 400 °C. In Kubelka–Munk calculation, (a) $R' = R_{\text{cat+NO-400}}/R_{\text{cat-400}}$; (b) $R' = R_{\text{cat+NH}_3\text{-400}}/R_{\text{cat-400}}$; (c) $R' = R_{\text{cat-NH}_3\text{+NO-400}}/R_{\text{cat+NH}_3\text{-400}}$.

To investigate the nature of active sites on CuO/cordierite-Al_2O_3(S) for the SCR reaction, the catalyst was exposed to a NH_3/Ar flow at 400 °C for NH_3 adsorption (Spectrum (a) in Fig. 7), and then to a NH_3 + NO + O_2/Ar flow for 25 min (Spectrum (b) in Fig. 7). The NH_3 was then removed from the feed and two Kubelka–Munk spectra were obtained in 5 min (Spectrum (c) in Fig. 7) and 25 min (Spectrum (d) in Fig. 7). Since the NH deformation peaks in the region of 1800–1100 cm^{-1} are weak and complex, the peaks of NH stretching in the region of 3500–2500 cm^{-1} are discussed below.

Three important features can be observed on Spectrum (b) in comparison to Spectrum (a): (1) decreases in peaks for NH_3/NH_2–NH_2 on Lewis acid sites (3341, 3282 and 3188 cm^{-1} (ν_{NH} of NH_3/NH_2)); (2) little change in peak for NH_4^+ on the cordierite

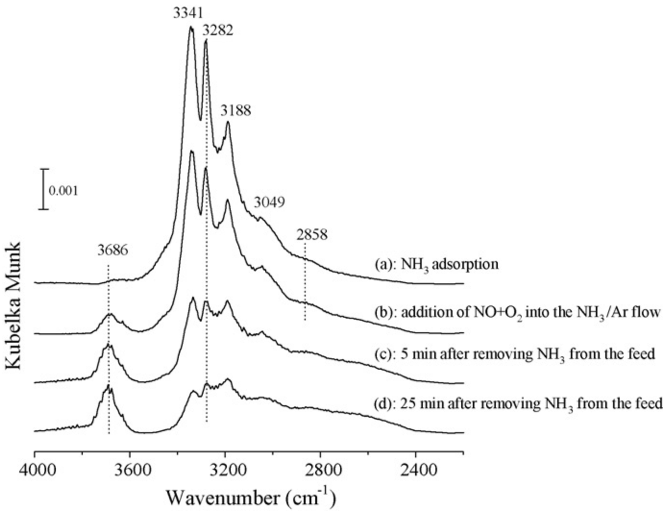

Fig. 7. DRIFTS spectra in Kubelka–Munk unit of CuO/cordierite-Al_2O_3(S) during transient response experiment at 400 °C. R' used for Kubelka–Munk calculation are described in detail in Section 2.4.3.

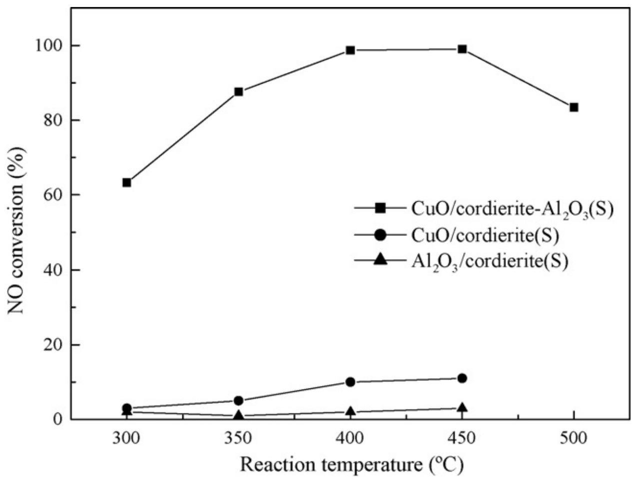

Fig. 8. NO conversions of the different samples at various temperatures [4].

(3049 cm^{-1}, ν_{NH}) and a slight increase in peak for NH_4^+ on alumina (2858 cm^{-1}, ν_{NH}); (3) appearance of a new peak assigned to –OH band (3686 cm^{-1}). These indicate that the SCR reaction mainly involves reactions of NH_3/NH_2 on Lewis acid sites, not NH_4^+ on Brønsted acid sites, and the H_2O produced in the SCR reaction transforms NH_3 to NH_4^+ [7,26].

A comparison of Spectra (b) and (c) indicates significant deceases in NH_3/NH_2–NH_2 on Lewis acid sites (3341, 3282 and 3188 cm^{-1}) and NH_4^+ on the cordierite (3049 cm^{-1}), little change in NH_4^+ on alumina (2858 cm^{-1}) and a slight increase in –OH band (3686 cm^{-1}). The depletion of ammonia species may result from their reactions with NO as well as from desorption. It has shown in Fig. 1 that NH_4^+ on the Brønsted sites is thermally less stable than NH_3/NH_2–NH_2 adsorbed on the Lewis sites, however, the depletion of NH_3/NH_2–NH_2 is far faster than that of NH_4^+ in Fig. 7. This suggests that a large number of NH_3/NH_2–NH_2 reacts with NO, which is also confirmed by the differences in Spectra (c) and (d).

The comparison of Spectra (c) and (d) further shows that the decreasing rate of the NH_3/NH_2–NH_2 peaks follows the order of 3341 > 3282 > 3188 cm^{-1}. As a result, the peak intensity in Spectrum (d) follows the order of 3188 > 3282 > 3341 cm^{-1}. This is different from the observations in TPD (Fig. 1, 3274 > 3336 > 3181 cm^{-1}) and suggests that NH_2–NH_2 on the copper species in $CuAl_2O_4$ (ν_{NH} of NH_2 at 3282 cm^{-1}) is the main source for the SCR reaction, whereas NH_3 on the other copper site (ν_{NH} of NH_3 at 3188 cm^{-1}) is probably inactive. It is surprise to see that the peaks of NH_4^+ (3049 and 2868 cm^{-1}), which disappears at 240 °C in the TPD, are still visible in Fig. 7. This suggests the formation of a large amount of NH_4^+ through interactions between the coordinated NH_3 and H_2O produced in the SCR. Since the NH_4^+ formed is on aluminum site, the NH_3 transformed to NH_4^+ should also be on the aluminum site. Therefore, the faster decrease in the peak at 3341 cm^{-1} (associated with aluminum site) can be attributed to transformation of the NH_3 species to NH_4^+, not to the SCR reaction.

3.4. Discussion to the activity test results

Fig. 8 restates steady-state NO conversions of CuO/cordierite-Al_2O_3(S), CuO/cordierite(S) and Al_2O_3/cordierite(S) reported in literature [4]. It is clear that CuO/cordierite-Al_2O_3(S) shows far higher SCR activities than CuO/cordierite(S) and Al_2O_3/cordierite(S), indicating that co-presence of CuO and Al_2O_3 is important for the SCR catalyst. This may be attributed to the increased surface area of the support after being coated with Al_2O_3, 0.7 m^2/g for the cordierite and 14.5 m^2/g for the cordierite-Al_2O_3, which results in a better dispersion of CuO and thus a high SCR activity. However, the higher activity of CuO/cordierite-Al_2O_3(S) may also be attributed to joint effects of aluminum and copper species in $CuAl_2O_4$: aluminum for NH_3 storage and copper for NH_3 activation to NH_2–NH_2, as evidenced earlier in this work. The very low SCR activities of Al_2O_3/cordierite(S) and CuO/cordierite(S) are results of limited abilities in NH_3 activation and NH_3 adsorption, respectively.

It should be noted that although the amount of NH_3 adsorbed on CuO/cordierite-Al_2O_3(S) is much less than that reported on CuO/Al_2O_3(S) [27], they show similar SCR activities under similar conditions. This suggests that NH_3 activation is more important than NH_3 adsorption for SCR over CuO/Al_2O_3 based catalysts.

4. Conclusions

Sulfated CuO/cordierite-Al_2O_3 catalyst has a high activity for SCR of NO at 350–500 °C. It contains both Lewis and Brønsted acid sites. The Lewis acidity is far stronger than the Brønsted acidity, and the coordinated ammonia on the Lewis sites are thermally more stable than the protonated ammonia on the Brønsted sites. There are at least two types of Lewis sites on the catalyst and the main one is on $CuAl_2O_4$. The aluminum species in $CuAl_2O_4$ is responsible for storage of NH_3 and the copper species for activation of NH_3 to NH_2–NH_2, which is the intermediate of the SCR reaction. NO cannot be adsorbed on the catalyst surface and the SCR reaction follows Eley–Rideal mechanism.

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