

## DeNO<sub>x</sub> performance and characteristic study for transition metals doped iron based catalysts

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**Abstract**—Novel, environmentally-benign catalysts for selective catalytic reduction of NO<sub>x</sub> were prepared by citric method through introducing transition metal elements (Ce, Cu and Co) into iron oxide. The physical-chemical properties of different catalysts were investigated by the characterization technologies like N<sub>2</sub>-physisorption, XRD, NH<sub>3</sub>/NO-TPD and H<sub>2</sub>-TPR. The results indicated that the introduction of transition metal elements increased the specific surface area and adsorption ability for reactants (NH<sub>3</sub> and NO<sub>x</sub>). The redox capacity for the doped catalysts was improved at the same time. These characteristics all contributed to the improvement of catalytic performance. The CoFeO<sub>x</sub> catalyst exhibited the widest temperature window for SCR reaction, and the CeFeO<sub>x</sub> catalyst showed the most obvious decline of NO<sub>x</sub> conversion with the elevation of temperature above 250 °C. Water vapor inhibited the SCR activity at low temperatures and relieved the decline of NO<sub>x</sub> conversion at higher temperatures. Meanwhile, the formation of N<sub>2</sub>O was inhibited. The pretreatment of SO<sub>2</sub> led to the sulfation of the active species for different catalysts. The decline of redox capacity and the reduction of active nitrate adsorbed species accounted for the serious loss of SCR activity at low temperatures. The abundant surface acid sites brought by the sulfation process might be the main reason for good SCR activity in the medium temperature range.

Keywords: Transition Metals, Iron, SCR, H<sub>2</sub>O, Sulfation

### INTRODUCTION

Selective catalytic reduction (SCR) with ammonia is the most efficient and economic technology for NO<sub>x</sub> removal that has been successfully applied for several decades in coal-fired power plants [1-4]. The most widely used commercial catalysts are vanadium-based catalysts like V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/TiO<sub>2</sub> [1,5-7]. The undesired oxidation of SO<sub>2</sub> [8] is an obvious drawback for this kind of catalyst. The toxicity of vanadium pentoxide to environment and human health led the wasted catalysts to being classified as hazardous waste and to be handled differently [9,10]; thus, many researchers are focusing on the development of new vanadium-free SCR catalysts.

The environmentally-benign iron based catalysts for selective catalytic reduction of NO<sub>x</sub> have attracted much attention. Based on the abundance of published researches, the manganese based catalysts and cerium-based catalysts exhibited great SCR activity under the clean condition without H<sub>2</sub>O and SO<sub>2</sub> [11-15]. The poor resistance to H<sub>2</sub>O and SO<sub>2</sub> was the main barrier for the application of these novel SCR catalysts in the real environment [16,17]. The low N<sub>2</sub> selectivity was another drawback for the manganese-

based catalysts [18]. Numerous studies have shown that the iron-based catalysts had better resistance to SO<sub>2</sub> in the medium temperature range. Kato et al. [19] studied the SCR performance of iron oxide-titanium oxide first and found that Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts exhibited high activity and selectivity over a temperature range of 350 °C-450 °C. The deep investigation found that the activity was enhanced with increase in the content of SO<sub>4</sub><sup>2-</sup> in the catalyst [20]. Liu et al. [21] reported a novel iron titanate catalyst which has excellent SCR activity, N<sub>2</sub> selectivity and H<sub>2</sub>O/SO<sub>2</sub> durability in medium temperature, and the mechanism study revealed that the SCR process mainly followed the Langmuir-Hinshelwood (L-H) mechanism in a relatively low temperature range (<200 °C) and the Eley-Rideal (E-R) mechanism at a relatively high temperature (>200 °C) [22]. In addition, Yang et al. [23] synthesized the Fe-Ti spinel catalyst that had excellent SCR activity and H<sub>2</sub>O/SO<sub>2</sub> durability at 300-400 °C. Ma et al. [24] compared the SCR activities of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/TiO<sub>2</sub> and other catalysts containing iron and sulfates and found that Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/TiO<sub>2</sub> catalyst exhibited the highest NO<sub>x</sub> conversion and lowest N<sub>2</sub>O selectivity. Fe-zeolite catalysts have attracted much attention in recent years and the investigations about the activities of different iron species [25], the influence of loading [26], hydrothermally ageing [27,28] and NO<sub>2</sub> in the feed gas [29] have been performed by many researchers. The abundant reports have proved that the iron-based catalysts exhibited a good ability to resist the SO<sub>2</sub> poison to a certain extent, and the introduction of other elements might improve the reaction activity according to the published [30-32].

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Most of the published papers investigated the supported catalysts with different supporters like  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and zeolites as mentioned above. To avoid the influence of the supporter, we hope to synthesize the bulk phase catalysts and investigate the mutual effect of iron and transition metal elements directly. The cerium and iron composite could be obtained by co-precipitation method with ammonia water as the precipitant [30]. However, the  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  ions could not be precipitated by ammonia water, because that  $\text{NH}_4^+$  could react with the corresponding cation species forming the complex ions. Using the alkali hydroxide as the precipitant will bring in the residual of alkali metal, which can lead to the poisoning of SCR catalysts. Therefore, we adopted the citric method that has been used successfully as the doping way [33,34]. In this paper, we prepared the iron-based catalysts doped by different transition metal elements (Ce, Cu and Co). The influence of different transition metal elements on the SCR activity was compared. The characterizations including  $\text{N}_2$ -physisorption, XRD,  $\text{NH}_3/\text{NO}$ -TPD and  $\text{H}_2$ -TPR were employed to analyze the physical-chemical properties of these modified catalysts. The resistance to  $\text{H}_2\text{O}$  and  $\text{SO}_2$  was investigated and the characterization analyses for the catalysts pretreated by  $\text{SO}_2$  were carried out to explore the deactivation reason.

## EXPERIMENTAL

### 1. Catalyst Preparation

The  $\text{MFeO}_x$  mixed oxide catalysts were prepared by the citric method. The iron nitrate nonahydrate with different transition metal nitrate (cerium nitrate hexahydrate, copper nitrate trihydrate and cobalt nitrate hexahydrate) were dissolved in deionized water first. The molar ratio of Fe and M (M=Ce, Cu and Co) was 9 : 1. The appropriate amount of nitric acid and citric acid was added into the solution, respectively. The molar ratio of metal components to citric acid to nitric acid was 1 : 1.5 : 1.5. The solutions were stirred at 80 °C for 5 h to form the gels. Then the gels were dried at 105 °C overnight and calcined in a muffle furnace at 400 °C for 3 h. The samples were pelleted, crushed and sieved to 40-60 mesh for performance evaluation and characterization. The catalysts doped by different transition metals are denoted as  $\text{MFeO}_x$  (M=Ce, Cu and Co). The single metal oxides ( $\text{FeO}_x$ ,  $\text{CeO}_x$ ,  $\text{CuO}_x$  and  $\text{CoO}_x$ ) were synthesized by the same method for comparison. The commercial  $\text{Fe}_2\text{O}_3$  (analytical reagent) was purchased from Sinopharm Chemical Reagent Co., Ltd and labeled as  $\text{Fe}_2\text{O}_3$  (AR). To investigate the influence of  $\text{SO}_2$  on the properties of different catalysts, the corresponding catalysts were pretreated under the condition with 1,000 ppm  $\text{SO}_2$  and 5 vol%  $\text{O}_2$  at 300 °C for 4 h. The pretreated catalysts are labeled as  $\text{MFeO}_x$ -S (M=Ce, Cu and Co).

### 2. Activity Test

SCR activity tests for different catalysts were conducted in a fixed-bed stainless steel reactor (i.d 10 mm). 1.5 mL catalysts with 40-60 mesh size were used for the performance test. The simulated flue gas consisted of 500 ppm NO, 500 ppm  $\text{NH}_3$ , 3 vol%  $\text{O}_2$  and  $\text{N}_2$  in balance. The total flow rate was 1.5 L/min (refers to 1 atm and 25 °C), which corresponded to a gas hourly space velocity (GHSV) of 60,000  $\text{h}^{-1}$ . When the resistance to  $\text{H}_2\text{O}$  was tested, the deionized water was injected into the preheating section by the micro syringe pump and then was vaporized and mixed with other

gas components. The concentrations of NO,  $\text{NO}_2$  and  $\text{O}_2$  in the outlet gas were measured online by the flue gas analyzer (NOVA PLUS, MRU, Germany), while the  $\text{N}_2\text{O}$  concentration was measured by a  $\text{N}_2\text{O}$  analyzer (G200, UK). The product was analyzed when the reaction system reached a steady state for 30 min. The  $\text{NO}_x$  conversion was calculated as follows:

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

$\text{NO}_x$  includes NO and  $\text{NO}_2$ .  $\text{N}_2\text{O}$  is classified as the undesired product.

A separate  $\text{NH}_3$  oxidation test was performed in a quartz reactor and the GHSV was the same as SCR activity test. Different catalysts (1 mL, 40-60 mesh) were used to oxidize 300 ppm  $\text{NH}_3$  in presence of 3 vol%  $\text{O}_2$  catalytically. Except for monitoring the  $\text{NO}_x$  and  $\text{N}_2\text{O}$ , the outlet concentration of  $\text{NH}_3$  was measured by ULTRAMAT6 analyzer (Siemens, Germany).

### 3. Catalyst Characterization

The  $\text{N}_2$  adsorption-desorption isotherms were obtained at -196 °C using a JW-BK112 instrument (Beijing JWGB Sci. & Tech. Co., Ltd., China). Prior to  $\text{N}_2$  adsorption, the catalyst samples were degassed at 250 °C for 5 h. The surface areas were determined by BET equation in 0.05-0.35 partial pressure range. Pore volumes and average pore diameters were determined by BJH method from the adsorption branches of the isotherms. The XRD measurements were conducted on a Rigaku D/max-RB Diffractometer (Japan,  $\text{Cu K}\alpha$  as radiation resource).

$\text{NH}_3$ -TPD and  $\text{NO}_x$ -TPD were carried out using FineSorb 3010D chemisorption analyzer (FINETEC instruments, China). Prior to TPD experiments, the samples (100 mg) were pretreated at 400 °C in a flow of helium (20 mL/min) for 1 h and cooled to 80 °C. Then the samples were exposed to a flow of 5 vol%  $\text{NH}_3/\text{N}_2$  or 5 vol%  $\text{NO}/\text{N}_2$  (20 mL/min) for 30 min, followed by He purge for another 1 h. Finally, the temperature was raised to 500 °C in He flow at the rate of 10 °C/min. The amount of ammonia or  $\text{NO}_x$  species desorbed from the catalysts was monitored by a thermal conductivity detector (TCD).

$\text{H}_2$ -TPR was also performed using the same instrument. Before the experiment, the catalysts (50 mg) were pretreated at 400 °C in a flow of Ar (20 mL/min) for 1 h and cooled to 50 °C. Then the temperature was raised linearly to 800 °C at the rate of 10 °C/min in a flow of 10% vol.  $\text{H}_2/\text{Ar}$  (20 mL/min). The  $\text{H}_2$  consumption was monitored by TCD.

*In situ* DRIFTS spectra were measured by an FTIR spectrometer (Thermo Nicolet 6700) equipped with a diffuse reflectance optics accessory. The catalysts were pretreated at 450 °C in a flow of 5 vol%  $\text{O}_2/\text{N}_2$  for 0.5 h and cooled to 100 °C. Thereafter, the background spectra were recorded. The 1 vol%  $\text{NH}_3/\text{N}_2$  mixed gas was passed over the catalysts for 0.5 h and then the system was purged by  $\text{N}_2$  for 1 h. The spectra were recorded by accumulating 32 scans with a resolution of 4  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

### 1. SCR Activity

First, we tested the SCR activity of single metal oxide and the

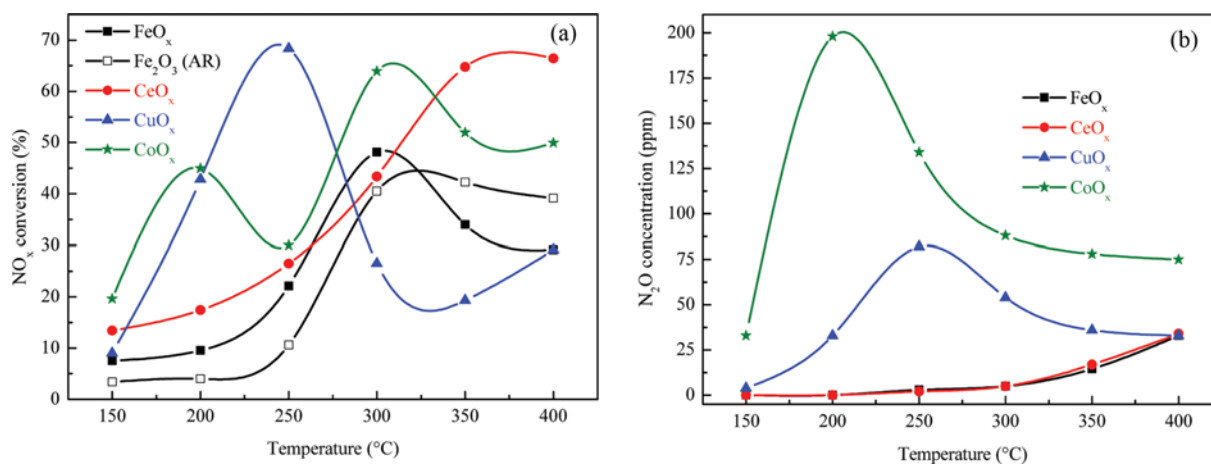


Fig. 1. NO<sub>x</sub> conversion (a) and N<sub>2</sub>O concentration (b) for single metal oxides as a function of temperature. Reaction condition: [NH<sub>3</sub>]=[NO]=500 ppm, [O<sub>2</sub>]=3 vol%, N<sub>2</sub> as balance, total flow rate=1.5 L/min and GHSV=60,000 h<sup>-1</sup>.

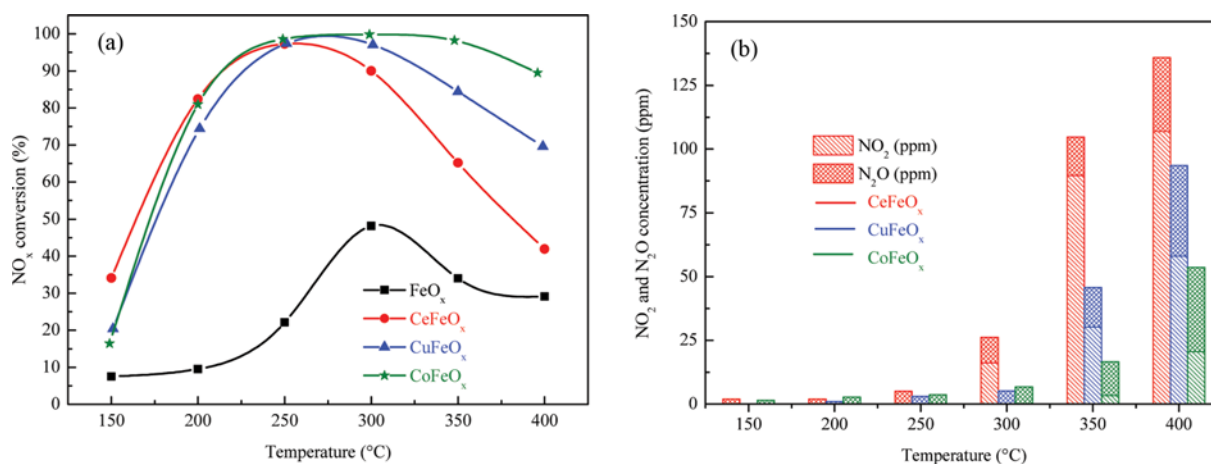


Fig. 2. NO<sub>x</sub> conversion (a), NO<sub>2</sub> and N<sub>2</sub>O concentration (b) for the different catalysts as a function of temperature. Reaction condition: [NH<sub>3</sub>]=[NO]=500 ppm, [O<sub>2</sub>]=3 vol%, N<sub>2</sub> as balance, total flow rate=1.5 L/min and GHSV=60,000 h<sup>-1</sup>.

results are shown in Fig. 1. Compared with the Fe<sub>2</sub>O<sub>3</sub> (AR), the FeO<sub>x</sub> sample exhibited the better catalytic performance at low temperature. However, the decrease of NO<sub>x</sub> conversion was more obvious for Fe<sub>2</sub>O<sub>3</sub> (AR) at higher temperature. The NO<sub>x</sub> removal efficiency increased monotonically with the increase of reaction temperature for CeO<sub>x</sub>. The NO<sub>x</sub> conversion increased rapidly to a maximum at 250 °C for CuO<sub>x</sub> sample and then decreased at higher temperature. The SCR activity for CoO<sub>x</sub> was interesting that there were two peaks of NO<sub>x</sub> reduction in different temperature range. Combining with the formation of N<sub>2</sub>O, we speculated that different reaction pathways took place at different temperature. The NO might be removed through Langmuir-Hinshelwood mechanism at 200 °C. The adsorbed nitrate species reacted with the adsorbed ammonia forming NH<sub>4</sub>NO<sub>3</sub> species, which could be reduced by NO to product N<sub>2</sub> and H<sub>2</sub>O or decompose to N<sub>2</sub>O and H<sub>2</sub>O directly [22,35]. The excellent activity of cobalt species for NO oxidation in the published papers [36-38] and the trend of N<sub>2</sub>O in the exhaust could support our speculation. When the reaction temperature rose, the stable nitrate species could not be formed. But the activation of

ammonia was enhanced and NO could be reduced by active ammonia species through Eley-Rideal mechanism. To sum up, FeO<sub>x</sub> and CeO<sub>x</sub> samples showed better N<sub>2</sub> selectivity, while the catalytic activity at low temperature was worse.

The SCR activity and NO<sub>2</sub>, N<sub>2</sub>O concentrations in the outlet for different doped catalysts are shown in Fig. 2. The SCR activity of complex oxides catalysts was different from that of those single metal oxide samples obviously, which indicated that there were synergistic effects existing between iron and transition metal elements. The addition of transition metal elements increased the SCR activity dramatically compared with FeO<sub>x</sub> and there was a deep increase between 150 °C and 200 °C for these modified catalysts. The temperature corresponding to the highest NO<sub>x</sub> conversion shifted from 300 °C to 250 °C and the deNO<sub>x</sub> efficiencies all exceeded 95% at 250 °C for the series of MFeO<sub>x</sub> catalysts. When the temperature reached 300 °C, the NO<sub>x</sub> conversion of CeFeO<sub>x</sub> and CuFeO<sub>x</sub> started to decrease. The degree of decline was enhanced with the increase of temperature and it was more serious for CeFeO<sub>x</sub> catalyst compared with the CuFeO<sub>x</sub> sample. The turning point for CoFeO<sub>x</sub> cat-

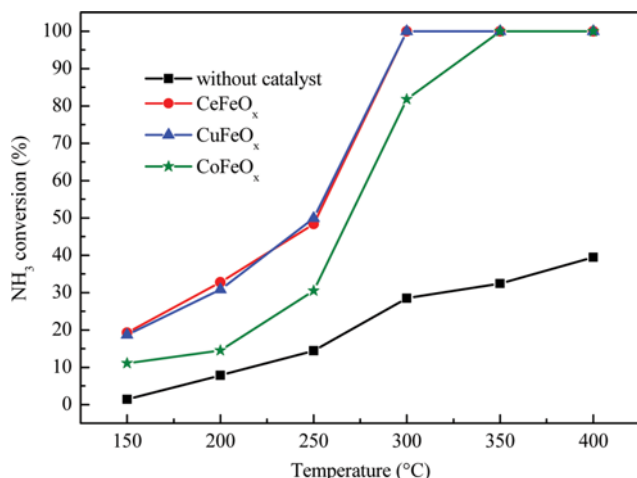


Fig. 3.  $\text{NH}_3$  conversion for the different catalysts as a function of temperature. Reaction condition:  $[\text{NH}_3]=300$  ppm,  $[\text{O}_2]=3$  vol%,  $\text{N}_2$  as balance, total flow rate=1.0 L/min and GHSV=60,000  $\text{h}^{-1}$ .

alyst was at 350 °C and its rate for decrease was smallest. The decrease of  $\text{NO}_x$  conversion at high temperature might be due to the over-oxidation of ammonia [21,32].

To confirm our speculation, a separate  $\text{NH}_3$  oxidation test was performed for these modified catalysts and the results are shown in Fig. 3. The blank test showed that ammonia was not stable in the presence of  $\text{O}_2$  at higher temperature. The existence of catalysts could improve the  $\text{NH}_3$  oxidation conversion. The  $\text{NH}_3$  oxidation activities for  $\text{CeFeO}_x$  and  $\text{CuFeO}_x$  catalysts were similar that the  $\text{NH}_3$  conversion increased rapidly when the temperature was over 250 °C and reached 100% at 300 °C. The  $\text{NH}_3$  conversion for  $\text{CoFeO}_x$  was lower and reached 100% at 350 °C. The temperature for complete  $\text{NH}_3$  oxidation was in accord with that for decline of  $\text{deNO}_x$  efficiency under SCR condition, which could support our speculation. Interestingly, there was almost no  $\text{N}_2\text{O}$  detected in the exhaust. Different proportions of  $\text{NO}$  and  $\text{NO}_2$  were monitored only at 400 °C.

It can be seen in Fig. 2(b) that only small amount of  $\text{N}_2\text{O}$  was detected at the temperature below 250 °C under SCR condition. The  $\text{NO}_2$  in the outlet appeared for  $\text{CeFeO}_x$  catalysts at 300 °C, which corresponded to the temperature that  $\text{NO}_x$  conversion started to decrease. The concentration of  $\text{NO}_2$  increased gradually with the temperature rising. Due to the over-oxidation ammonia,  $\text{NO}$  could not be reduced without enough reductant ( $\text{NH}_3$ ) and then was oxidized to  $\text{NO}_2$ . This phenomenon indicated the good  $\text{NO}$  oxidation performance for the doped catalysts. The  $\text{N}_2\text{O}$  formation in the temperature range investigated was similar for the different catalysts, and the concentration of  $\text{N}_2\text{O}$  reached the maximum (approximately 30 ppm) at 400 °C. Combined with the results of  $\text{NH}_3$  oxidation, we think that the  $\text{N}_2\text{O}$  came from the unselective catalytic reduction of  $\text{NO}$  instead of direct  $\text{NH}_3$  oxidation.

## 2. Catalyst Characterization

### 2-1. $\text{N}_2$ Physisorption and XRD

The structural parameters of the different catalysts are listed in Table 1. It can be seen that the addition of transition metals increased

Table 1. Structural parameters of different catalysts

Sample	BET surface area ( $\text{m}^2/\text{g}$ )	Total pore volume ( $\text{cm}^3/\text{g}$ )	Average pore diameter (nm)
$\text{FeO}_x$	19.32	0.287	51.34
$\text{CeFeO}_x$	130.81	0.244	6.76
$\text{CuFeO}_x$	37.93	0.172	19.23
$\text{CoFeO}_x$	40.70	0.241	18.86

the specific surface areas. The physical structures showed diverse changes for the novel catalytic materials with different doped elements. The specific surface area of the  $\text{FeO}_x$  sample was smallest and its pore was mainly macropore. The average pore diameter decreased for the doped catalysts and more mesoporous structure appeared. The  $\text{CeFeO}_x$  catalyst had the smallest average pore diameter and biggest BET surface area, while the  $\text{CuFeO}_x$  and  $\text{CoFeO}_x$  catalysts had similar physical structural parameters. According to the atomic radii proposed by Slater [39], it is easy to find that the iron, copper and cobalt have a similar atomic radius (Fe: 0.14 nm; Cu: 0.135 nm and Co: 0.135 nm), while the atomic radius of cerium is 0.185 nm. The obvious difference between the atomic radius of Ce and Fe might lead to more crystal distortion. The smallest average pore diameter of  $\text{CeFeO}_x$  was a valid proof for this deduction, and these small pore structures enlarged the specific surface area for the catalyst. The increase of specific surface area and adjustment of pore structure both could contribute to the improvement of catalytic performance.

Fig. 4 shows the XRD profiles of different catalysts. For  $\text{FeO}_x$  catalyst, the crystal  $\text{Fe}_2\text{O}_3$  was detected obviously, corresponding to the standard card (PDF 89-0597) in JCPDS. After the introduction of transition metals, the position and intensity of diffraction peaks for the doped catalysts changed significantly. Apart from the typical diffraction peak at 33.12° for crystal  $\text{Fe}_2\text{O}_3$ , most diffraction peaks were attributed to the formation of maghemite  $\text{Fe}_{21.333}\text{O}_{32}$  (PDF 83-0112). The transformation of the main crystal form indicated that the addition of transition metals affected the physical-

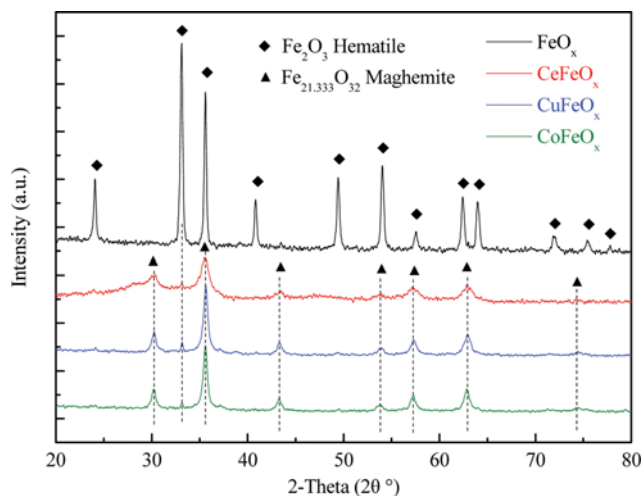


Fig. 4. XRD profiles for the different catalysts.

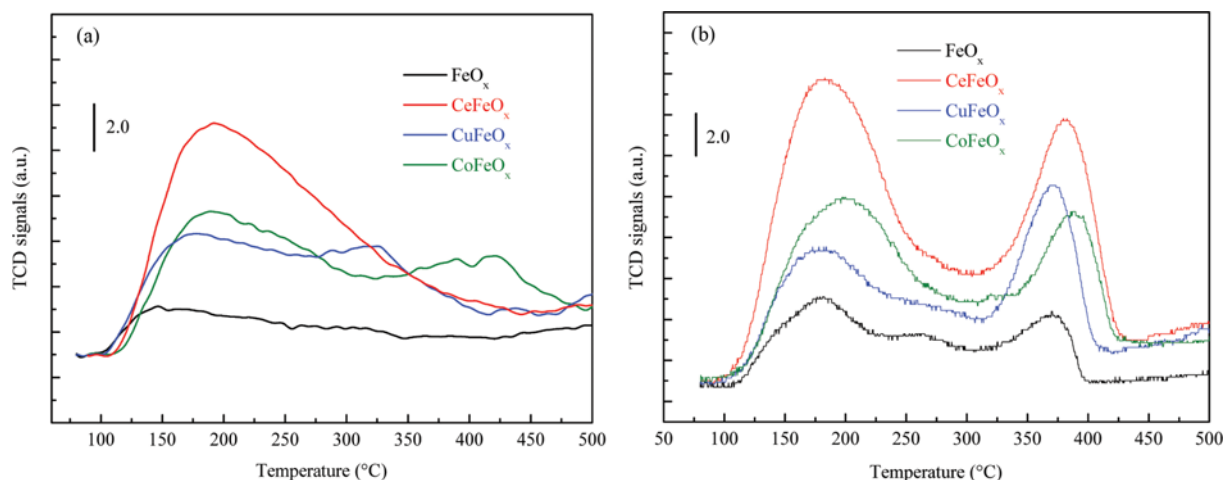


Fig. 5. NH<sub>3</sub>-TPD and NO-TPD profiles for the different catalysts.

chemical characteristic of iron-based materials and more crystal defect existed on the doped catalysts. Comparing these materials, the weakest diffraction peaks was for CeFeO<sub>x</sub> catalyst, which might be because the bigger atomic radius for cerium element reduced the degree of crystallization. There were no crystal diffraction peaks for the added transition metal oxides, which suggested that they were dispersed well on the surface of catalysts.

### 2-2. NH<sub>3</sub>-TPD and NO-TPD

According to the numerous investigations on the iron-based SCR catalysts, the adsorbed ammonia species and nitrate species showed reaction activity at different temperatures [22,23,40]. The adsorption of reactants on the surface of catalysts is a very important factor for the SCR performance of novel catalysts. The NH<sub>3</sub>-TPD and NO-TPD profiles for the different catalysts are shown in Fig. 5. It is easy to find that the addition of transition metals clearly increased the adsorbing capacity of the reactants. The bigger specific surface area was a reason for the increase of adsorption ability. However, the amount of reactants was out of proportion with the BET surfaces, which indicated that the chemical properties changed by the doping of transition metal elements. The CeFeO<sub>x</sub> catalyst exhibited the best adsorption capacity for NH<sub>3</sub> and NO<sub>x</sub>. The excellent oxygen storage ability of cerium contributed to the adsorption and activation of the reactants, which could explain the great oxidation performance for ammonia and NO during the activity test process. The broad peak between 350 °C and 450 °C in NH<sub>3</sub>-TPD profile showed that more strong Lewis acid sites existed on the surface of CoFeO<sub>x</sub> catalyst, and the desorption temperature for different nitrate species was higher than that of the other two modified catalysts, which indicated that the thermal stability for adsorbed ammonia and nitrate species was better for CoFeO<sub>x</sub> catalyst. This characteristic of CoFeO<sub>x</sub> catalyst prevented the over-oxidation of ammonia at high temperature, leading to the better SCR activity. Combining with the result of activity test, we speculated that there was a relation between the thermal stability of adsorbed ammonia and the ammonia oxidation ability of the novel catalysts.

### 2-3. H<sub>2</sub>-TPR

The redox capacity is another critical property for the selective

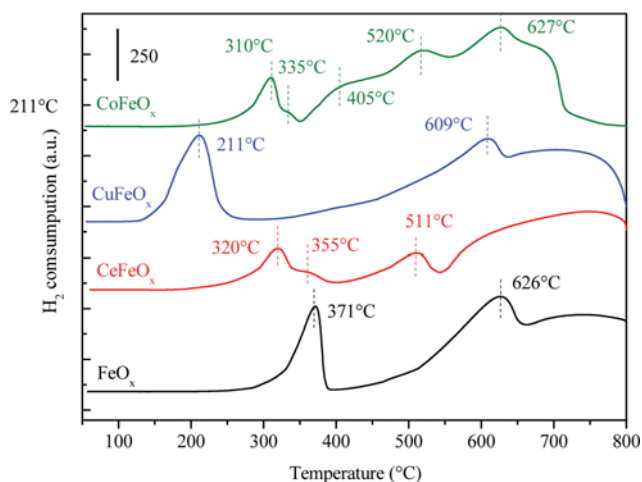


Fig. 6. H<sub>2</sub>-TPR profiles for the different catalysts.

catalytic reduction of NO with ammonia. Temperature-programmed reduction (TPR) technology was used to investigate the reducibility of the different catalysts, and the corresponding curves are shown in Fig. 6. The SCR reaction was operated below 500 °C, so the oxidation-reduction reaction that happened on the different catalysts during the SCR reaction may be only related to the reduction of low temperature. Therefore, we focused on the analysis of reduction peaks at low temperature. The first reduction temperature at 371 °C for FeO<sub>x</sub> was attributed to the sequential reduction of highly dispersive Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> [21,24]. The broad reduction peaks above 500 °C were attributed to the further reduction of Fe<sub>3</sub>O<sub>4</sub>, FeO, crystallized and bulk iron oxides [21,31]. Three different reduction peaks were found for CeFeO<sub>x</sub> catalyst. As reported, the reduction peak at 511 °C was due to the reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> [41]. The reduction peak at 355 °C corresponded to the shift of peak at 371 °C for FeO<sub>x</sub>. The new peak at 320 °C was caused by the strong interaction between FeO<sub>x</sub> and CeO<sub>x</sub> and could be assigned to the superimposed reduction of active cerium ions and iron ions [42]. The sole reduction peak at 211 °C for CuFeO<sub>x</sub> catalyst at low temperature was due to the overlap for the reduction of highly dispersed

copper oxides and iron oxides [32,43,44], which indicated the close interaction between Cu and Fe species existed. There were various reduction peaks for  $\text{CoFeO}_x$  catalyst, suggesting that different oxide forms existed. The first and second reduction peaks at 310 °C and 335 °C were superimposed by the reduction of highly dispersed  $\text{Co}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ , which were both lower than the single component samples [45]. The reduction peaks at 405 °C and 520 °C were attributed to the overlapped reduction of  $\text{CoO}$ ,  $\text{FeO}$  and crystallized iron species [31,37]. Different from the other catalysts,  $\text{CoFeO}_x$  sample was almost totally reduced below 800 °C. We speculated that the addition of cobalt as the adjacent subgroup element of iron greatly impacted the physical-chemical property of iron oxides.

Compared with the  $\text{FeO}_x$  catalyst, the introduction of Ce, Cu and Co all decreased the reduction temperature of active iron species, and the interaction between the doped elements and iron increased the redox capacity for the modified catalysts, contributing to the improvement of SCR activity.

### 3. Effect of $\text{H}_2\text{O}$ and $\text{SO}_2$

The effects of water vapor on the  $\text{NO}_x$  conversion and  $\text{N}_2\text{O}$  for-

mation of the different catalysts are shown in Fig. 7. Clearly, the existence of  $\text{H}_2\text{O}$  inhibited the SCR activity at low temperature. The  $\text{NO}_x$  conversion of  $\text{CuFeO}_x$  and  $\text{CoFeO}_x$  decreased from 74.4%, 81.0% to 26.0% and 23.0% at 200 °C, respectively, while the denitration efficiency of  $\text{CeFeO}_x$  could still keep at 49.0% at 200 °C. The inhibition of  $\text{H}_2\text{O}$  was reversible for all the doped catalysts, and the original catalytic performance could be recovered as the addition of water vapor was stopped [46,47]. As the reaction temperature rose, the degree of inhibition was reduced. The  $\text{NO}_x$  conversion at 250 °C in presence of  $\text{H}_2\text{O}$  was close to that at 200 °C in absence of  $\text{H}_2\text{O}$ . The temperature for turning point of  $\text{NO}_x$  conversion shifted from 300 °C to 350 °C and the decrease of SCR activity at high temperature for  $\text{CuFeO}_x$  and  $\text{CeFeO}_x$  was weakened dramatically. The suppression of adsorption and activation of reactants (ammonia and nitric oxide) was the main reason for the loss of activity at low temperature. The inhibition for over-oxidation of ammonia contributed to the activity improvement at high temperatures.

The  $\text{NO}_2$  was detected at 300 °C for  $\text{CeFeO}_x$  catalyst under the

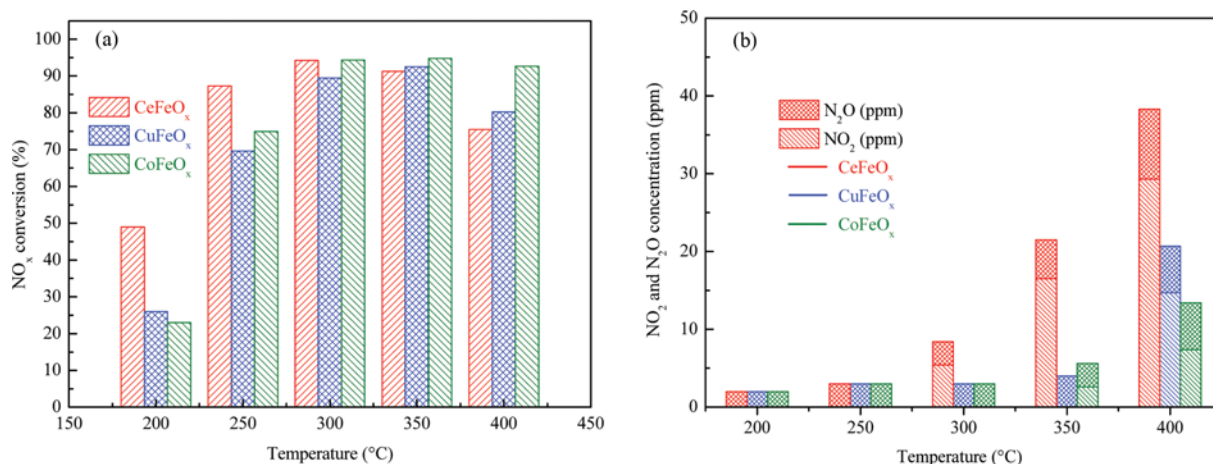


Fig. 7.  $\text{NO}_x$  conversion (a),  $\text{NO}_2$  and  $\text{N}_2\text{O}$  concentration (b) for the different catalysts as a function of temperature. Reaction condition:  $[\text{NH}_3]=[\text{NO}]=500$  ppm,  $[\text{O}_2]=3$  vol%,  $[\text{H}_2\text{O}]=5$  vol%,  $\text{N}_2$  as balance, total flow rate=1.5 L/min and GHSV=60,000  $\text{h}^{-1}$ .

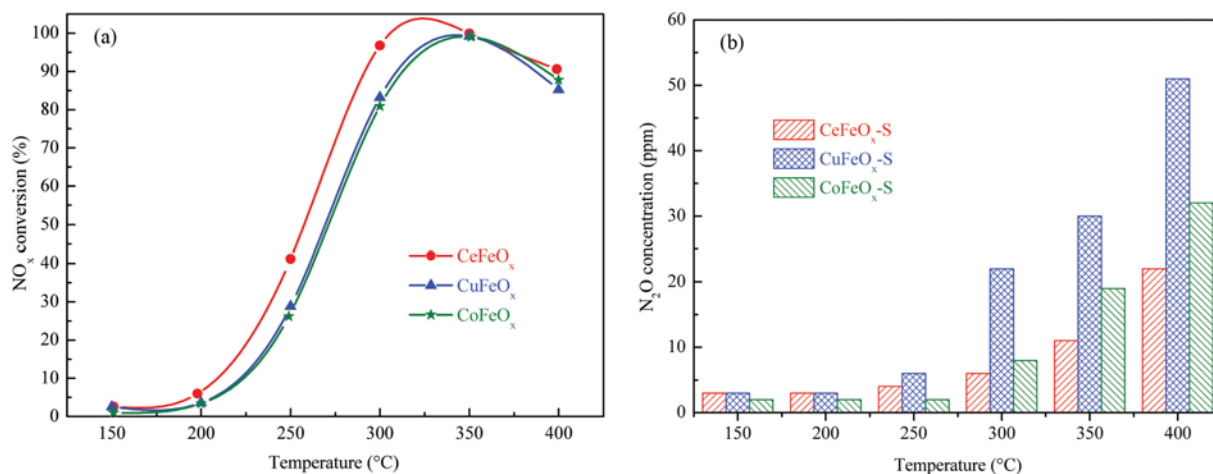


Fig. 8.  $\text{NO}_x$  conversion (a) and  $\text{N}_2\text{O}$  concentration (b) for the different catalysts pretreated by  $\text{SO}_2$  as a function of temperature. Reaction condition:  $[\text{NH}_3]=[\text{NO}]=500$  ppm,  $[\text{O}_2]=3$  vol%,  $\text{N}_2$  as balance, total flow rate=1.5 L/min and GHSV=60,000  $\text{h}^{-1}$ .

wet condition, which was in agreement with the phenomenon in absence of H<sub>2</sub>O. However, the concentration of NO<sub>2</sub> decreased significantly (107 ppm at 400 °C in absence of H<sub>2</sub>O vs. 29 ppm at 400 °C in presence of H<sub>2</sub>O). The influence for CuFeO<sub>x</sub> catalyst was similar to that for CeFeO<sub>x</sub> and the NO<sub>2</sub> was obvious only at 400 °C. The N<sub>2</sub>O concentration for different modified catalysts kept in the same level and the existence of water vapor inhibited the formation of N<sub>2</sub>O. Below 10 ppm N<sub>2</sub>O was detected for these catalysts at 400 °C.

The SO<sub>2</sub>-pretreated catalysts exhibited the different reaction activity in the temperature range investigated and the influence brought by the pretreatment of SO<sub>2</sub> was irreversible. The reaction activity at low temperatures was lost almost as shown in Fig. 8. The CuFeO<sub>x</sub> and CoFeO<sub>x</sub> catalysts showed the close NO<sub>x</sub> conversion at different temperature and NO<sub>x</sub> removal efficiency above 80% was only obtained between 300 °C and 400 °C. The NO<sub>x</sub> conversion for CeFeO<sub>x</sub> catalyst was slightly higher than the others at the same temperature. It is interesting that there was no NO<sub>2</sub> in the outlet even at 400 °C, which indicated that the SO<sub>2</sub>-pretreated catalysts lost the ability for NO oxidation. The trend for N<sub>2</sub>O formation of different catalysts was in accordance with the fresh catalysts that the N<sub>2</sub>O concentration increased with the elevation of reaction temperature. However, the order for N<sub>2</sub>O concentration changed. The SO<sub>2</sub>-pretreated CuFeO<sub>x</sub> catalyst produced the most N<sub>2</sub>O by-product above 300 °C, which was more than the corresponding fresh catalyst.

#### 4. Characterization for Catalysts Pretreated by SO<sub>2</sub>

To confirm the reason for the impacts brought by the pretreatment of SO<sub>2</sub> on the different modified catalysts, temperature-programmed desorption (NH<sub>3</sub>/NO-TPD) and temperature-programmed reduction (H<sub>2</sub>-TPR) technologies were carried out for the SO<sub>2</sub>-pretreated catalysts. The change of adsorption ability and reducibility could be obtained compared with the fresh catalysts in Section 2.

##### 4-1. NH<sub>3</sub>-TPD and NO-TPD

The NH<sub>3</sub>/NO-TPD profiles for the SO<sub>2</sub>-pretreated catalysts are shown in Fig. 9. Compared with Fig. 5, the amount for NH<sub>3</sub> adsorbed species increased dramatically for the SO<sub>2</sub>-pretreated cata-

lysts. There was a big broad peak between 100 °C and 500 °C for CeFeO<sub>x</sub>-S catalysts. The NH<sub>3</sub>-TPD profile of SO<sub>2</sub>-pretreated CoFeO<sub>x</sub> catalyst was similar to that of the fresh sample, and the temperature for the second desorption peak shifted towards higher temperature. The SO<sub>2</sub>-pretreated CuFeO<sub>x</sub> catalyst exhibited some new special desorption peaks, which might be attributed to the desorption of ammonia species adsorbed on copper sulfate. Combined with the change of SCR activity, the total amount of surface acid sites was not the determinant for NO<sub>x</sub> removal. It can be seen that there was only one desorption peak for NO<sub>x</sub> adsorbed species of these SO<sub>2</sub>-pretreated catalysts. The pretreatment of sulfur dioxide in presence of oxygen inhibited the absorption of nitrate species, especially bidentate nitrate and bridging nitrate with better thermal stability. The sulfated catalysts did not show enough NO<sub>x</sub> conversion in the temperature range for desorption of nitrate adsorbed species, which suggested that the nitrate adsorbed species did not have reaction activity for NO<sub>x</sub> removal. The same conclusion was obtained by Liu et al. [48] on the FeTiO<sub>x</sub> catalyst, that the active nitrate species could not form effectively owing to the strong acidity of sulfate species on iron sites.

Based on the change of adsorption capacity for NH<sub>3</sub> and NO<sub>x</sub> species, it could be concluded that sulfur dioxide bonded with the surface of different catalysts strongly during the pretreatment process and some reaction might happen between SO<sub>2</sub> and the surface active species in presence of excess O<sub>2</sub>.

##### 4-2. H<sub>2</sub>-TPR

The SO<sub>2</sub>-pretreated catalysts exhibited the different H<sub>2</sub>-TPR profiles compared with the fresh catalysts as shown in Fig. 10. It was obvious that all the initial reduction temperature shifted towards the higher temperature and the amount of H<sub>2</sub> consumption for the first reduction peak increased dramatically. The first reduction peak for CeFeO<sub>x</sub>-S and CoFeO<sub>x</sub>-S catalysts appeared at 492 °C and 410 °C respectively and they were overlapped by the reduction peaks for different species. The surface sulfate species were reduced by hydrogen firstly and then the corresponding metal oxides were reduced immediately. As the temperature continued increasing, the profile of H<sub>2</sub> consumption became similar with that of fresh catalysts. The CuFeO<sub>x</sub>-S catalyst showed two distinctive reduction

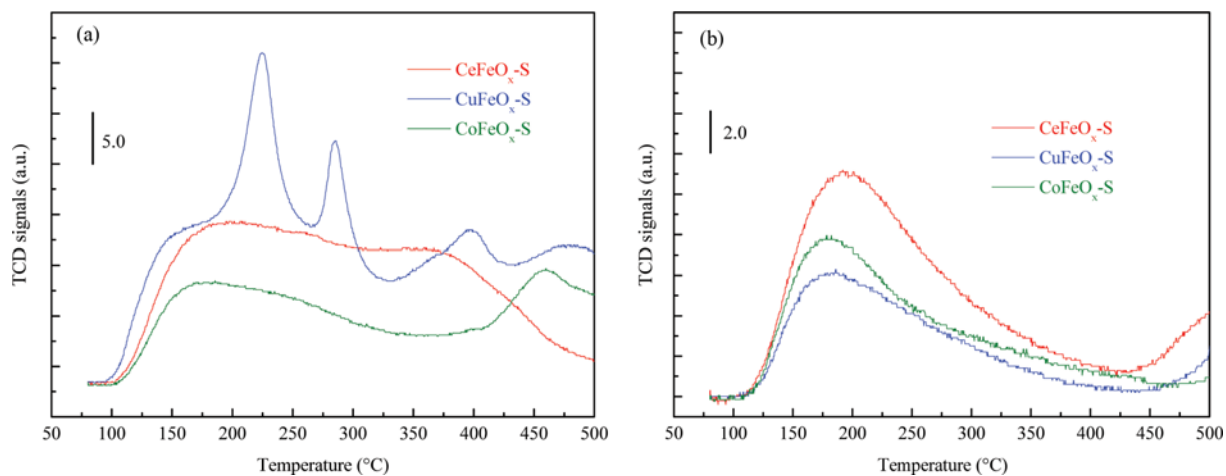


Fig. 9. NH<sub>3</sub>-TPD and NO-TPD profiles for the SO<sub>2</sub>-pretreated catalysts.

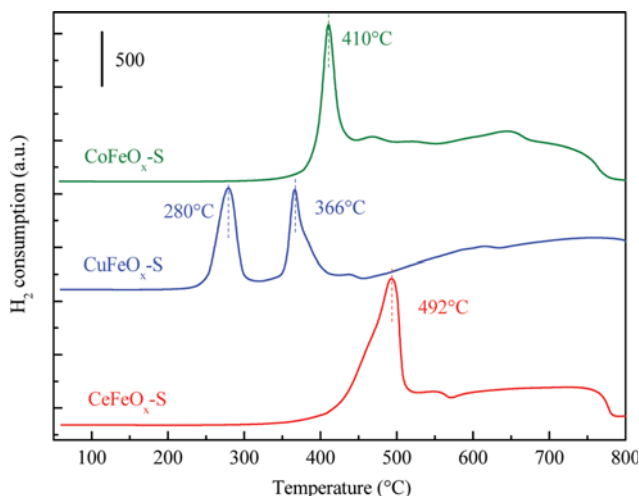


Fig. 10.  $H_2$ -TPR profiles for the  $SO_2$ -pretreated catalysts.

peaks and the pretreatment of  $SO_2$  might separate the reduction process for copper oxides and iron oxides. The first reduction peak at  $280^\circ C$  was attributed to the superimposed reduction of the sulfate species on  $CuO_x$  and highly dispersed copper oxides, while the second reduction peak at  $366^\circ C$  was assigned to the reduction of the sulfate species on iron oxides and corresponding iron oxides. We deduced that the sulfation of active species reduced the redox capacity of different catalysts and the reduction for surface sulfate accounted for the most of  $H_2$  consumption.

#### 4-3. IR Spectra

Interestingly, the pretreatment of  $SO_2$  increased the acid sites for the modified catalysts, which did not improve the catalytic performance. Due to the defect of TCD detector for identifying the type of acid sites, the change for different kind of acid sites could not be obtained from  $NH_3$ -TPD profiles. The *in situ* DRIFT spectra recorded for  $CeFeO_x$  and  $CeFeO_x-S$  catalysts at  $100^\circ C$  are shown in Fig. 11. After  $NH_3$  adsorption and  $N_2$  purge, the  $CeFeO_x$  catalyst

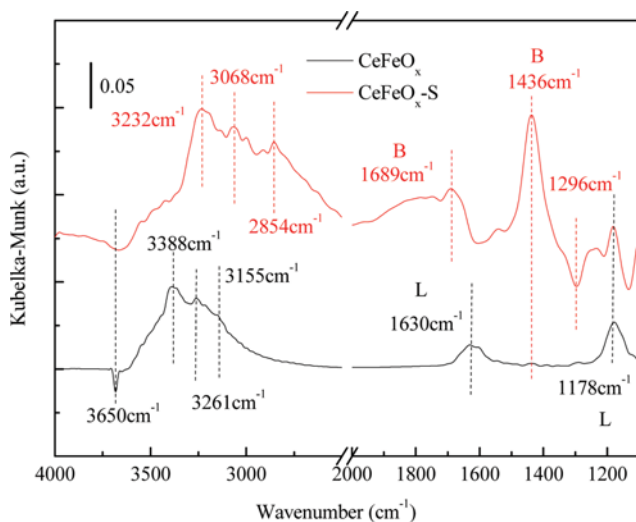


Fig. 11. DRIFT spectra for the fresh and  $SO_2$ -pretreated  $CeFeO_x$  catalysts.

was mainly covered by coordinated  $NH_3$  bound to Lewis acid sites ( $1,178\text{ cm}^{-1}$  for  $\delta_s NH_3$  and  $1,630\text{ cm}^{-1}$  for  $\delta_{as} NH_3$ ) [22,40]. There was almost no ionic  $NH_4^+$  bound to Brønsted acid sites on the surface of  $CeFeO_x$  catalyst. The bands at  $3,100\text{--}3,400\text{ cm}^{-1}$  ( $3,155$ ,  $3,261$  and  $3,380\text{ cm}^{-1}$ ) were attributed to N-H stretching vibration modes for the coordinated  $NH_3$  and the negative band at  $3,650\text{ cm}^{-1}$  was due to the consumption of the surface O-H stretching [22,23]. The spectrum for  $CeFeO_x-S$  catalyst was different with that for the fresh sample. The intensity of IR bands for the coordinated  $NH_3$  on the Lewis acid sites was weakened and strong IR bands for ionic  $NH_4^+$  bound to Brønsted acid sites ( $1,436\text{ cm}^{-1}$  for  $\delta_{as} NH_4^+$ ,  $1,689\text{ cm}^{-1}$  for  $\delta_s NH_4^+$  and  $3,068\text{ cm}^{-1}$ ,  $2,854\text{ cm}^{-1}$  for N-H stretching vibration) appeared obviously [40,49]. The results indicated the increase of amount of acid sites, which was in agreement with  $NH_3$ -TPD results. The negative IR band at  $1,296\text{ cm}^{-1}$  was near the  $1,309\text{ cm}^{-1}$  for the sulfate and bisulfate species reported by Xu et al. [17]. The bands at  $1,689\text{ cm}^{-1}$  and  $1,436\text{ cm}^{-1}$  for  $NH_4^+$  originated from the ammonia bound to the sulfate and bisulfate species and the coverage of ionic  $NH_4^+$  led to the emergence of the negative band at  $1,296\text{ cm}^{-1}$ .

The IR spectra confirmed the occurrence of sulfation of active species. As reported, it is generally accepted that NO could be reduced by  $NH_3$  through the Langmuir-Hinshelwood (L-H) mechanism and Eley-Rideal (E-R) mechanism [22,49]. The adsorption and activation of ammonia is the key step for the E-R mechanism, while the formation of active nitrate species is recognized as the important step for the L-H mechanism. The sulfation of active species lost the excellent redox capacity for these catalysts, judging from the TPR-profiles. The activation of coordinated  $NH_3$  was limited for the pretreated catalysts. And at the same time, the formation of active nitrate species was inhibited. The two pathways for  $NO_x$  removal were both cut off for these catalysts pretreated by  $SO_2$ . So, in accordance with the experimental result, the SCR activity at low temperature decreased dramatically. The abundant surface acid sites and high reaction temperature kept the good  $NO_x$  conversion in the medium temperature range. We speculated  $NO_x$  was reduced by  $NH_3$  through the route of E-R mechanism for the sulfated catalysts.

## CONCLUSION

Environmentally-benign iron based catalysts for selective catalytic reduction of  $NO_x$  have attracted considerable attention. We have investigated the de $NO_x$  performance and physical-chemical properties of the novel  $MFeO_x$  mixed oxides catalysts ( $M=Ce, Cu, Co$ ) prepared by citric method. The characterization results indicated that the introduction of transition metal elements increased the specific surface area and adsorption ability for reactants ( $NH_3$  and  $NO_x$ ). The redox capacity for the doped catalysts was improved at the same time. These characteristics all contributed to the improvement of catalytic performance. The  $CoFeO_x$  catalyst exhibited the widest window temperature for SCR reaction. The  $CeFeO_x$  catalyst showed the most obvious decrease of  $NO_x$  conversion with the elevation of temperature, and excellent NO oxidation efficiency was observed at higher temperatures. The declining degree of  $NO_x$  conversion at higher temperatures was in line with the sequence of

thermal stability for ammonia adsorbed species on the different catalysts. Water vapor inhibited the SCR activity at low temperatures and relieved the decline of NO<sub>x</sub> conversion at higher temperatures. Meanwhile, the formation of N<sub>2</sub>O was inhibited. The pretreatment of SO<sub>2</sub> led to the sulfation of the active species for different catalysts. The decline of redox capacity and the reduction of active nitrate adsorbed species accounted for the serious loss of SCR activity at low temperatures. The abundant surface acid sites brought by the sulfation process might be the main reason for good SCR activity in the medium temperature range.

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