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CrO_x-CeO_2 二元氧化物表面 NO 的 NH_3 催化还原反应机理

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摘要: 利用原位漫反射红外光谱法研究了 473 K 下在 CrOx-CeO_2 二元氧化物表面 NO 的 NH_3 催化还原反应的机理。研究了 CrOx-CeO_2 二元氧化物表面在反应过程中的表面吸附物种。为了更加清晰的了解反应过程,在 SCR 反应过程中分别切断 NH_3 和 NO 的气流,并采集了所生成的原位漫反射红外光谱图,通过研究以上结果得出结论:当前状态下的 SCR 反应过程可能服从 E-R 机理。

关键词: Cr_2O_3; CeO_2; SCR; NO_x; 原位红外
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Reaction Mechanism of NH_3-Selective Catalytic Reduction for NO on CrO_x-CeO_2 Binary Oxide

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Abstract: *In-situ* Diffuse Reflectance Infrared Fourier Transform (*In-situ* DRIFT) Spectroscopy was employed to investigate the reaction mechanism of NH_3-Selective Catalytic Reduction (SCR) upon NO on CrO_x-CeO_2 binary oxide at 473 K. The surface adsorbed species on the CrO_x-CeO_2 binary oxide during the SCR reaction were analyzed. To elucidate the reaction process more precisely, we cut off the NH_3 and NO flow, respectively, in the SCR reaction and collected the resulting *in-situ* DRIFT spectra. The results indicate that the SCR reaction process might follow the Eley-Rideal (E-R) mechanism.

Key words: Cr_2O_3; CeO_2; SCR; NO_x; *In-situ* DRIFT

Nitrogen oxide (NO_x) has been one of the most important pollutants in China nowadays. NO_x generated from mobile sources (gasoline or diesel engines) and stationary sources (fossil-fueled power plant and steel enterprises) causes serious atmospheric pollution and gives rise to secondary organic aerosol which is responsible for the notorious haze in China recently. High-temperature waste gas containing NO_x could be successfully treated with V-W-Ti Selective Catalytic Reduction (SCR) catalyst. NO_x in low-temperature flue gases, however, is still a problem to be solved because the temperatures of flue gases are too low to light on the SCR over common catalysts. To solve the problem, many researchers devoted themselves to searching for new SCR catalyst with good low temperature catalytic ability[1-11]. Among all past studies on new catalyst candidates, CrO_x-CeO_2 binary oxide is scarcely investigated and its catalytic

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mechanism is seldom studied[12].

In this study, we investigate the NH_3-SCR reaction mechanism for NO over CrO_x-CeO_2 binary oxide at 473 K with *In-situ* Diffuse Reflectance Infrared Fourier Transform (*In-situ* DRIFT) Spectroscopy. The spectra of catalyst surface after adsorption with NH_3+Air, NO+Air and NH_3+NO+Air were collected and analyzed. To elucidate the reaction process more precisely, we cut off the NH_3 and NO flow, respectively, from the SCR reaction flow (NH_3+NO+Air) and collected the resulting *in-situ* DRIFT spectra. The results show that the SCR reaction process on the CrO_x-CeO_2 binary oxide might follow the E-R mechani sm.

1 Experimental

1.1 Chemicals

Cerium nitrate [$Ce(NO_3)_3 \cdot 6H_2O$], chromium nitrate [$Cr(NO_3)_3 \cdot 9H_2O$] and aqueous ammonia (30wt%) were purchased from Beijing Reagent Co., Ltd.. Spectroscopically pure bromide potassium (KBr) was purchased from Sigma-Fluka. The water used in the present work was deionized water with R>18 MΩ. Calibrating gases containing NO (2 500 $\mu L \cdot L^{-1}$+N_2 balance) and NH_3 (2 500 $\mu L \cdot L^{-1}$+N_2 balance) along with synthetic air were purchased from Beijing Huayuan Gas Chemical Industry Co., Ltd..

1.2 Experimental procedure

1.2.1 CrO_x-CeO_2 binary oxide preparing

Based on our previous work, we prepared the CrO_x-CeO_2 binary oxide with best SCR ability (n_{Cr}:n_{Ce}=1:3)[12]. Aqueous cerium nitrate and chromium nitrate solution (overall metal concentration 0.05 mol·L^{-1}) were precipitated with aqueous ammonia under vigorous stirring until pH=10. The resulting slurry was stirred for 2 h and washed thoroughly with deionized water before being centrifuged and dried. Calcining the as-made solids at 480 ℃ for 4 h gave rise to atrovirens powder denoted as Cr25Ce75. Pure CeO_2 and Cr_2O_3 were also prepared with the similar routine, and the resulting powders are denoted as CeO2 and Cr2O3 respectively.

1.2.2 Sample characterization

The powder XRD pattern of Cr25Ce75, CeO2 and Cr2O3 were recorded in 2θ from 10° to 90° with a scanning step of 0.033 4° on PANalytical X′Pert PRO X-ray diffraction using Ni filtered Cu $K\alpha$(λ=0.154 18 nm) radiation at 40 kV and 30 mA. The *in-situ* DRIFT spectra of the samples were obtained using a Bruker Vertex 70 spectrometer equipped with diffuse reflectance accessory (PIKE Technologies). To minimize the contamination of the sample powder on the porous crucible, 20 mg KBr powder layer was laid under the sample layer (Fig.1).

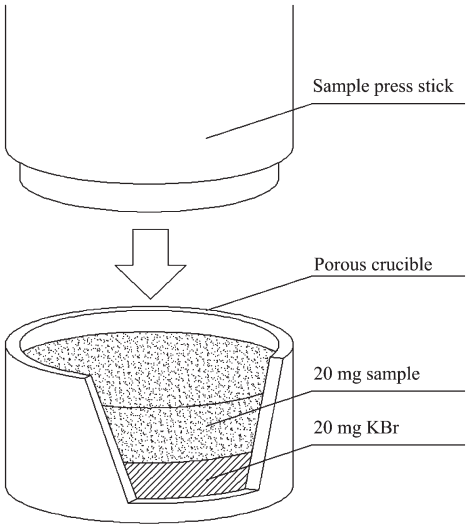


Fig.1 Filling of the crucible

Before the analysis, the sample cell was heated to 480 ℃ under synthetic air flow (30 mL·min^{-1}) for 2 h. The sample cell was then cooled in synthetic air to 200 ℃ and the background was collected. Then, the stream of mixture between NO calibrating gas (2 500 $\mu L \cdot L^{-1}$ 15 mL·min^{-1}) and synthetic air (30 mL·min^{-1}) was injected into the sample cell and the resulting spectra were obtained to analyze the surface adsorption species aroused by NO. The similar routine was used to obtain the spectra caused by NH_3 adsorption on the surface of the samples. In the SCR process, the mixture of NO calibrating gas (2 500 $\mu L \cdot L^{-1}$, 15 mL·min^{-1}), NH_3 calibrating gas (2 500 $\mu L \cdot L^{-1}$, 15 mL·min^{-1}) and syntheic air (30 mL·min^{-1}) was injected into the sample cell after pre-heating the sample in synthetic air at 480 ℃ for 2 h and collecting the background when the samples cell was

cooled to 200 ℃ in synthetic air. Once the corresponding spectra were stable and collected, the NO or NH_3 stream was cut off, the resulting spectra were recorded for further discussion.

2 Results and discussion

2.1 XRD analysis of samples

The powder XRD patterns of Cr25Ce75, Cr2O3 and CeO2 are shown in Fig.2. The pattern of sample CeO2 shown the cubic fluorite strucre of ceria, at the same time, reflection ascribable to Cr_2O_3 could be found in the diffraction profile of Cr2O3. The diffraction profiles of Cr25Ce75, however, is very similar to that of CeO2 without any characteristic peaks of Cr_2O_3. It could also be seen that compared with the XRD patterns of CeO2, the diffraction line of Cr25Ce75 shifts to higher angles which corresponds to decrease of the lattice constant. The formation of solid solution composed of CeO_2 and Cr_2O_3 in Cr25Ce75 is implied by this phenomenon[12-13]. It is highly possible that the valance state of chromium is 3 in Cr25Ce75.

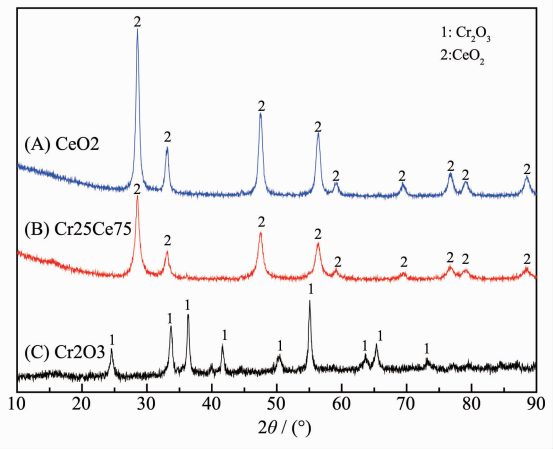
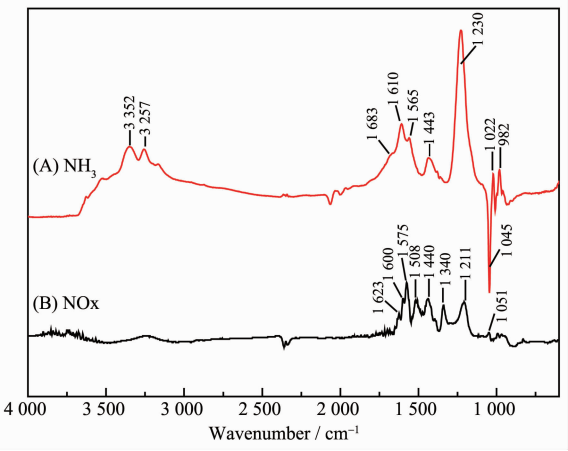


Fig.2　XRD patterns of samples

2.2 NH_3 and NO adsorption onto Cr25Ce75

The *in-situ* DRIFT spectra of Cr25Ce75 surface treated with NH_3 and NO calibrating gas are shown in Fig.3. The strong adsorption bands at 1 230, 1 565 and 1 610 cm^{-1} are attributed to the adsorbed NH_3 species coordinated with the electron-deficient metal atoms (Lewis acid sites)[14-15]. The adsorption bands at 3 352 and 3 257 cm^{-1} are assigned to the stretching vibrations of weakly adsorbed ammonia species[16]. The strong and sharp negative peak centered at 1045 cm^{-1} is scarcely reported in earlier studies. In the work of Casapu et al.[14], the NH_3 treated ternary oxide (Nb-Mn-Ce) exhibits negative peak in DRIFT spectra but the phenomenon is not discussed. Because many studies concerning the IR spectra of chromium speies attribute the band around 1 010 cm^{-1} to the Cr=O group [17-20], here we reasonably assign the negative peak centered at 1 045 cm^{-1} to the elimination of Cr=O group on the surface of Cr25Ce75 because of the ammonia adsorption. Formation of NH_4^+ at Brönsted acid sites causes the band located at 1 443 cm^{-1} and 1 683 cm^{-1} [14]. Lewis acid sites on the surface of Cr25Ce75 make the main contribution in NH_3 adsorption.



A: NH_3 species+Air and B: NO species+Air

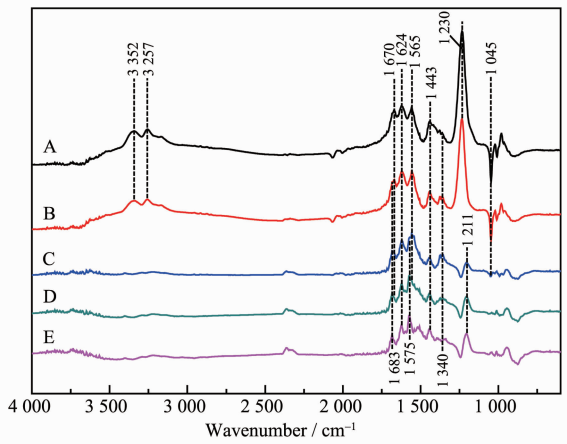
Fig.3　DRIFT spectra of Cr25Ce75 surface adsorbed species

Fig.3B exhibits the adsorption spectrum of Cr25Ce75 surface treated with NO+Air. The band at 1 211 cm^{-1} is due to the symmetric NO_2 vibration of chelating nitrite (NO_2^-)[21]. Bidentate and unidentate nitrate bands could be observed at 1 600, 1 575, 1 440, 1 340 cm^{-1} [22-23]. The bridging bidentate nitrate at 1 623 cm^{-1} is due to disproportionation of NO[24-25]. It could be seen clearly that under the present conditions, NO+O_2 mixture could generate both nitrite and nitrate adsorption on the catalysts surface.

2.3 *In-situ* DRIFT spectra of reacted species between NO and NH_3 on Cr25Ce75

To elucidate the reaction mechanism of the catalytic reduction for NO with NH_3 on Cr25Ce75, the

DRIFT spectra of Cr25Ce75 surface adsorbed NH_3+NO+Air flow were recorded (Fig.4A). Very similar to the spectrum of Cr25Ce75 treated with NH_3+Air, the intense adsorption band caused by NH_3 adsorbed on Lewis acid sites (1 230, 1 565, 3 352, 3 257 cm^{-1})[14-16] and negative peak attributed to vanishment of Cr=O (1 045 cm^{-1}) are clearly observed. Consequently, we could reasonably conclude that coordinated NH_3 species to Lewis acid sites are the main adsorbed group on the Cr25Ce75 surface during the SCR reaction. The bands centered at 1 443 and 1 670 cm^{-1} could be roughly sorted as adsorption of NH_4^+ group on Brönsted acid sites[14]. The adsorption peak located at 1 624 cm^{-1}could be attributed to another coordinated NH_3 species on Lewis acid sites [25]. Slightly different from those in the spectrum of Cr25Ce75 treat with NH_3 (trace A, Fig.3), the adsorption bands of NH_4^+ on Brnsted acid sites (1 443 and 1 670 cm^{-1}) in the spectrum of Cr25Ce75 treated with NH_3 +NO +Air mixture (Fig.4A) becomes more intense (compared with those bands of coordinated NH_3 on Lewis acid sites). The infared bands of nitrite and nitrate species is not observed.



A: NH_3+NO+Air mixture; B: NH_3 cutoff for 1 min; C: NH_3 cutoff for 3 min; D: NH_3 cutoff for 5 min; E: NH_3 cutoff for 10 min (at 473 K)

Fig.4 DRIFT spectra of Cr25Ce75 surface adsorbed species

To further clarify to SCR reaction process, the NH_3 was cut off from the SCR-reaction gas flow. The resulting spectra at different cut off times were recorded and are shown in Fig.4 as B (NH_3 cut off for 1 min), C(NH_3 cut off for 3 min), D(NH_3 cut off for 5 min) and E (NH_3 cut off for 10 min). It could be seen that positive peaks at 1 230, 3 352, 3 257 cm^{-1} and negative peak at 1 045 cm^{-1} diminish and disappear as the time goes by. The band centered at 1 565 cm^{-1} also sightly shifts to 1 575 cm^{-1} which might be resulted by the comsumption of coordinated ammonia species (1 565 cm^{-1}) and simultaneous appearance of unidentate nitrates. At the same time, the band at 1 670 cm^{-1} sightly shifts to 1 683 cm^{-1}, which might be caused by NH_4^+ ion with less symmetry[26]. In C, D and E, a new adsorption band at 1 211 cm^{-1} is observed indicating the formation of chelating nitrite (NO_2^-)[21]. The coexistence of bands at 1 443cm^{-1} and 1 683 cm^{-1} in E of Fig.4 indicates that some NH_4^+ ions on the Cr25Ce75 could not be consumed by NO which implies the lower reactivity of NH_4^+ at Brönsted acid sites than that of coordinated NH_3 at Lewis acid sites on the present catalyst. The band centered at 1 624 cm^{-1} in C, D, E of Fig.4 might be caused by disproportionation of adsorbed NO.

From all the above results, we conclude that the NH_3 SCR reaction for NO on Cr25Ce75 follows the Eley-Rideal (E-R) type mechanism, as previously established[27-30]. Firstly, the ammonia molecules are adsorbed by Cr=O groups on the catalyst surface which generates -NH_2 groups (postive peak at 1 230 cm^{-1}), as a result, Cr=O groups are eliminated (negative peak at 1 045 cm^{-1}); secondly, the NO in reactant gas reacts with -NH_2 and genertates NH_2NO intermediate which decomposes into N_2 and H_2O imediately. Because nitrite species (1 624 cm^{-1}) are also observed, we could not completely rule out the slim possiblity that some -NH_2 reacts with adsorbed NO on the catalyst surface. Because the decomposing reaction of NH_2NO intermediate is very fast, no characteristic peaks of NH_2NO is observed[31].

The proposed mechanism is illustrated by Fig.5. In step Ⅰ, the unshared electron-pair of nitrogen atom in NH_3 intereacts with the vacant 3*d* orbital of Cr atom. In step Ⅱ, NO in gas reacts with the -NH_2 groups and gives rise to NH_2NO intermediate. In step Ⅲ, NH_2NO molecule decomposes into N_2+H_2O, and

Cr(Ⅱ)-OH is formed (corresponding to the broad peak around 3 400 cm^{-1}). Cr(Ⅱ) could be easily and rapidly oxidized by the active surface oxygen of CeO_2. Simutaneously, O_2 in air takes effect in the reoxidation of Ce^{3+} to Ce^{4+} to complete the redox cycle (step Ⅳ). According to this proposed mechanism, the optimium molar ratio between Cr and Ce is 1/3. Our ealier work proves that the binary oxide of CrO_x and CeO_2 achieved the best SCR catalytic results when their molar ratio is n_{Cr}/n_{Ce}=1/3. That former results might be an evidence for the plausibleness of the mechanism proposed above.

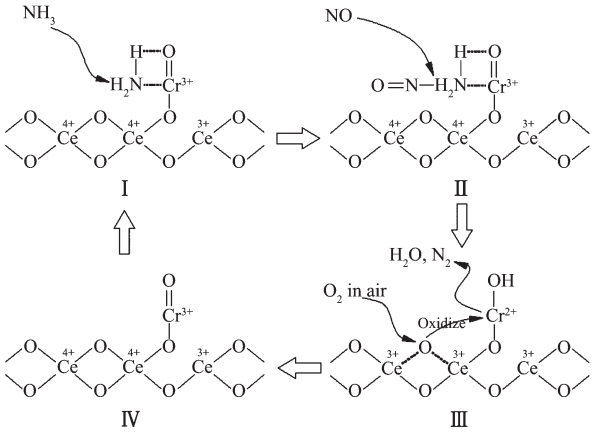
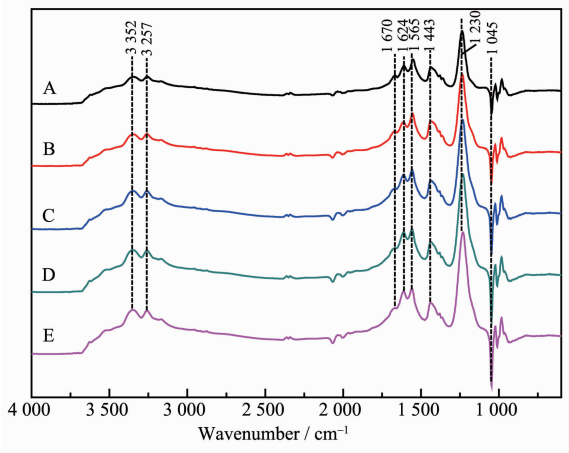


Fig.5　Proposed SCR reaction mechanism on Cr25Ce75

We also conducted other experiments in which the NO was cut off from the SCR-reaction gas flow. The relative spectra with different cut off times were recorded and are shown in Fig.6B (NO cut off for 1 min), C(NO cut off for 3 min), D(NO cut off for 5 min) and E (NO cut off for 10 min). As is shown by Fig.6, the profiles of all the spectra are almost completely identical which further proves that the present adsorbed groups on the surface of Cr25Ce75 during SCR reaction are mainly aroused by NH_3 adsorption. The band at 1 624 cm^{-1} might be either unresolved surface species aroused by NH_3-adsorption or surface nitrite species that could not be consumed by ammonia adsorbed on Lewis acid sites.



A: NH_3+NO+Air mixture; B: NO cutoff for 1min; C: NO cutoff for 3 min; D: NO cutoff for 5 min; E:NO cutoff for 10 min (at 473 K)

Fig.6　DRIFT spectra of Cr25Ce75 surface adsorbed

3　Conclusions

From all the results obtained by *in-situ* DRIFT method on the binary oxide (CrO_x-CeO_2), we conclude that the NH_3-SCR reaction for NO on the surface of the catalyst is in compliance with the Eley-Rideal type mechanism at the present temperature (473 K). In another word, ammonia is strongly adsrobed on Cr=O group and generates coordinated NH_3 molecules. The H-abstraction force of Cr=O causes deformation on NH_3 molecules and generates -NH_2 groups which reactes with gasous NO and gives rise to NH_2NO intermediate. The NH_2NO intermediate decomposes immediately and reduces the Cr(Ⅲ)=O to Cr(Ⅱ)-OH (corresponding to broad peak around 3 400 cm^{-1}). The active surface oxygen from CeO_2 could oxidize the Cr(Ⅱ)-OH to regenerate Cr=O. O_2 in the reactant gas takes effect in the reoxidation of Ce^{3+} to Ce^{4+} to complete the redox cycle.

In summary, the obvious SCR catalytic ability of Cr25Ce75 could be attributed to the combination of good redox ability of CeO_2 and proper acidity of Cr=O group which confirms the speculation of our earlier work[12].

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