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Supercritical water syntheses of transition metal-doped CeO₂ nano-catalysts for selective catalytic reduction of NO by CO: An *in situ* diffuse reflectance Fourier transform infrared spectroscopy study

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ABSTRACT

In the present study, we synthesized CeO₂ catalysts doped with various transition metals (M = Co, Fe, or Cu) using a supercritical water hydrothermal route, which led to the incorporation of the metal ions in the CeO₂ lattice, forming solid solutions. The catalysts were then used for the selective catalytic reduction (SCR) of NO by CO. The Cu-doped catalyst exhibited the highest SCR activity; it had a *T*₅₀ (i.e., 50% NO conversion) of only 83 °C and a *T*₉₀ (i.e., 90% NO conversion) of 126 °C. Such an activity was also higher than in many state-of-the-art catalysts. *In situ* diffuse reflectance Fourier transform infrared spectroscopy suggested that the MO_x-CeO₂ catalysts (M = Co and Fe) mainly followed an Eley-Rideal reaction mechanism for CO-SCR. In contrast, a Langmuir-Hinshelwood SCR reaction mechanism occurred in CuO-CeO₂ owing to the presence of Cu⁺ species, which ensured effective adsorption of CO. This explains why CuO-CeO₂ exhibited the highest activity with regard to the SCR of NO by CO.

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1. Introduction

Nitrogen oxides (NO_x)—which are generated by many combustion processes, both stationary and mobile—are considered primary atmospheric pollutants [1,2]. The emission of NO_x into the atmosphere can cause series environmental issues, including photochemical smog, acid rain, and ozone depletion [3,4]. Currently, the selective catalytic reduction (SCR) of NO_x is considered one of the most efficient techniques for the removal of stationary-source NO_x [5–7]. The SCR of NO using CO as a

reducing agent has been studied extensively in recent decades because NO and CO coexist in many industrial exhaust gases [8–10]. However, this approach presents several challenges such as ensuring low-temperature activation, resistance to O₂ and SO₂, and durable operation.

Noble metals have been used extensively as efficient catalysts for the CO-SCR reaction. However, owing to the high cost and poor resistance to sulfur/phosphate of noble metals [11], much effort has been devoted to developing transition metal oxide catalysts, and cerium-based catalysts have attracted the

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greatest interest. CeO₂ is an essential rare earth oxide with excellent oxygen storage capacity and redox behavior [12,13], which may be attributed to the flexible transformation between valence states (Ce⁴⁺ ↔ Ce³⁺) [14–16]. Many transition metals have been introduced into the CeO₂ lattice to modify its physical and chemical properties for various catalytic applications [17]. The synergistic effect arising from such modifications has become a primary focus in the catalysis research community [18–22]. Yao *et al.* [23] reported that a doped CeO₂ (Ce_xSn_{1-x}O₂) exhibited superior catalytic performance compared with undoped CeO₂ owing to the greater number of catalytic domains; Ma *et al.* [24] obtained a highly active Ce_xCu_{1-x}O₂ catalyst characterized by the presence of an intergrowth system comprising imperfect monoclinic CuO and cubic crystal CeO₂.

In the present study, we prepared a series of MO_x-CeO₂ catalysts (M = Co, Fe, or Cu) using a supercritical water (sc-H₂O) hydrothermal route [25]. The catalysts were subsequently characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area measurement, and hydrogen temperature-programmed reduction (H₂-TPR). The CO-SCR reaction activity of the catalysts was evaluated using *in situ* diffuse reflectance Fourier transform infrared spectroscopy (DRFTIR). We expect that this work will provide an in-depth understanding of the effectiveness of transition metal-doped CeO₂ catalysts in the CO-SCR reaction for NO removal.

2. Experimental

2.1. Catalyst preparation

The transition metal-doped catalysts were prepared in our laboratory using a three-pump hydrothermal flow system (CHFS). The reactor, tubing, and components were made from grade 316 stainless steel (Swagelok™). The apparatus (Fig. S1) consisted of a metal salt solution high-performance liquid chromatography (HPLC) pump (P2), a base solution HPLC pump (P3), and a water HPLC pump (P1). Deionized water was pre-heated to the appropriate temperature (500 °C) by pumping it through an electric coil (2.5 kW). The deionized water was then brought into contact with a metal salt solution containing Ce(NO₃)₃·6H₂O (0.1 mol·L⁻¹) and M(NO₃)_x·yH₂O (0.02 mol·L⁻¹), and a flow of NaOH solution (1 mol·L⁻¹) at a mixing point (a 1/4" counter-current mixer that was assisted by a 500 °C band heater), whereupon there was rapid co-precipitation of the crystalline products. The aqueous suspension was cooled using a water jacket, passed through a 7-μm in-line filter, and collected from the exit of a back-pressure regulator (BPR). Flow rates of 7.5, 7.5, and 30 mL·min⁻¹ were used for the metal salt solution, the base solution, and the water stream, respectively. The system pressure was maintained at approximately 23.0 MPa. Solids were recovered by centrifuging the suspension and freeze-drying to yield the final products.

2.2. Measurement of catalytic activity

The SCR of NO by CO was conducted in a fixed-bed quartz tubular reactor with a thermocouple at its center. The catalysts

were pre-treated in a N₂ flow at 500 °C for 1 h before each test. The catalytic activity of each 40–60 mesh catalyst (2.2 mL) was examined and the experiments were performed at 60 to 300 °C. The inlet gas comprised NO (600 ppm), CO (1200 ppm), and N₂ (the balance), and had a gas hourly space velocity (GHSV) of 40,000 h⁻¹. NO, NO₂, and O₂ concentrations were monitored using a Testo 350 flue gas analyzer. NO conversion and selectivity were evaluated as follows:

$$\text{NO conversion (\%)} = ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}) / [\text{NO}]_{\text{in}} \times 100\%$$

$$\text{N}_2 \text{ selectivity (\%)} = (1 - 2[\text{N}_2\text{O}]_{\text{out}} / ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}})) \times 100\%$$

where the “in” and “out” subscripts indicate the inlet and outlet concentrations of NO/N₂O in the steady state, respectively.

2.3. Characterization of the catalysts

2.3.1. XRD and BET

XRD patterns were recorded using a Rigaku D/Max RA diffractometer with Cu-K_α radiation (λ = 0.15418 nm) at 40 kV and 150 mA. All XRD patterns were obtained with scattering angles (2θ) ranging from 10° to 80° at a step size of 0.026°. The crystal phases of the catalysts were identified according to the Joint Committee on Powder Diffraction Standards (JCPDS) database.

The BET surface areas (BETs) were determined using N₂ physisorption at -196 °C using Micrometrics ASSP 2020 equipment. Prior to N₂ adsorption, each catalyst was degassed for 2 h under vacuum at 200 °C.

2.3.2. H₂-TPR

H₂-TPR was conducted in TP-5089 equipment (Tianjin Xianquan Industry and Trade Development Co., Ltd.); before each test, the catalysts (0.05 g) were maintained at 400 °C for 1 h and purged with 3% O₂/He gas at a flow rate of 50 mL·min⁻¹, then cooled to 100 °C. Subsequently, they were preheated at 100 °C for 40 min, then further heated to 900 °C at a rate of 10 °C·min⁻¹ while purging with 5% H₂/N₂ gas at a flow rate of 35 mL·min⁻¹. The variation in H₂ concentration was recorded using a thermal conduction detector (TCD).

2.3.3. *In situ* DRFTIR study

Fourier-transform infrared spectroscopy (FTIR) spectra were acquired using an *in situ* DRFTIR cell equipped with a gas flow apparatus. The DRFTIR measurements were obtained using ZnSe windows coupled to Bruker tensor 27 FTIR spectrometers. Inside the DRFTIR cell, the catalysts were pretreated in a He atmosphere at 300 °C for 2 h, then cooled to 100 °C. The background spectrum was obtained using flowing He, and was subtracted from the spectrum of each catalyst.

3. Results and discussion

3.1. XRD and BET measurements

The phase identities and purities of the M-doped CeO₂ catalysts (M = Co, Fe, or Cu) were evaluated by XRD. As shown in Fig. 1, all the catalysts displayed distinct XRD reflections at approximately 28.6°, 33.2°, 47.5°, 56.4°, and 76.9° for cubic

Fig. 1. (a) XRD patterns of catalysts comprising $\text{FeO}_x\text{-CeO}_2$, $\text{CoO}_x\text{-CeO}_2$ and CuO-CeO_2 ; (b) The respective magnified patterns.

fluorite CeO_2 (PDF-ICDD81-0792). No extra peaks attributable to FeO_x , CoO_x , or CuO species were observed. This may have been because the ultrafine transition metal oxides were highly dispersed throughout the CeO_2 , or because the CeO_2 lattice was fully doped with the metal ions [17,26]. All the catalysts had a higher 2θ shift than pure CeO_2 (see the magnified patterns in Fig. 1(b)). This suggests that the transition metal ions were all incorporated into the CeO_2 lattice and formed solid solutions, consistent with previous reports [27,28]. Such incorporations led to the shrinkage of the CeO_2 lattice because each metal ion had a lower ionic radius than Ce^{4+} (0.094 nm) [29,30]. The BET surface areas of the $\text{FeO}_x\text{-CeO}_2$, $\text{CoO}_x\text{-CeO}_2$ and CuO-CeO_2 catalysts were 147.6, 86.5 and 106.8 $\text{m}^2\cdot\text{g}^{-1}$, respectively.

3.2. Measurement of catalytic activity

As shown in Fig. 2(a), the pure CeO_2 exhibited the lowest SCR activity measured in the absence of light; its T_{50} (i.e., 50% NO conversion) was approximately 233 °C and its T_{90} (i.e., 90% NO conversion) was approximately 300 °C. The doping of CeO_2 with transition metals greatly improved its SCR activity, and the CuO-CeO_2 catalyst had the highest SCR activity of the catalysts investigated (i.e., a T_{50} of only 83 °C and a T_{90} of approximately 126 °C). The synergic interaction between the transition

metals and the cerium accounts for the improvement in performance. Compared with many state-of-the-art catalysts, which usually have a T_{50} in the range 200–300 °C [31], the CuO-CeO_2 catalyst exhibited superior SCR activity with regard to the reduction of NO by CO. We prepared a CuO-CeO_2 catalyst with an identical composition using a conventional hydrothermal route for comparison. As shown in Fig. S2, the catalyst produced by the supercritical water hydrothermal (sc- H_2O) route exhibited much higher SCR activity than that produced by the conventional hydrothermal route (ht- CuO-CeO_2), further confirming the superiority of the sc- H_2O route. The sequence of SCR activity was: $\text{FeO}_x\text{-CeO}_2 < \text{CoO}_x\text{-CeO}_2 < \text{CuO-CeO}_2$. This was not consistent with the surface areas of the catalysts, which suggests that surface area is not the crucial determinant of CO-SCR reactivity. Fig. 2(b) shows N_2 selectivity in CuO-CeO_2 and CeO_2 catalysts. The CuO-CeO_2 catalyst also exhibited a superior N_2 selectivity; its T_{50} was approximately 147 °C and its T_{90} was approximately 179 °C with regard to N_2 selectivity.

3.3. H_2 -TPR analyses

Fig. 3 illustrates H_2 -TPR profiles of the catalysts in the temperature range 100–800 °C. Pure CeO_2 had two H_2 consumption peaks at approximately 470 and 700 °C, which we ascribed

Fig. 2. (a) NO conversion over $\text{FeO}_x\text{-CeO}_2$, $\text{CoO}_x\text{-CeO}_2$, CuO-CeO_2 , and CeO_2 catalysts; and (b) N_2 selectivity (%) of CuO-CeO_2 and sc- CeO_2 in the SCR of NO by CO.

Fig. 3. H_2 -TPR profiles of catalysts comprising FeO_x-CeO_2 , CoO_x-CeO_2 and $CuO-CeO_2$.

to the reduction of surface and bulk CeO_2 , respectively [32]. The CoO_x-CeO_2 catalyst exhibited a series of consumption peaks in the range 100–350 °C. Apparently, various cobalt oxides, including CoO , Co_3O_4 , and Co_2O_3 , coexist in this catalyst. The FeO_x-CeO_2 catalyst exhibited three peaks centered at approximately 356, 535, and 789 °C. We attributed the latter two peaks to CeO_2 , whereas we believe the former peak was due to the reduction of $Fe-O-Ce$ [33]. The CuO_x-CeO_2 catalyst had the highest redox potential of the catalysts investigated; we observed two H_2 consumption peaks at approximately 142 and 158 °C, which we ascribed to the reduction of finely dispersed CuO and $Cu-O-Ce$, respectively [32,34–37]. Apparently, the redox potentials obtained from the H_2 -TPR analysis followed the sequence $FeO_x-CeO_2 < CoO_x-CeO_2 < CuO-CeO_2$, which was in accordance with the corresponding activity measurements.

3.4. In situ DRFTIR measurements of NO and/or CO adsorption and reaction

3.4.1. NO adsorption on MO_x-CeO_2 over time

Fig. 4 illustrates the DRFTIR spectra of NO adsorption onto the MO_x-CeO_2 catalysts ($M = Co, Fe, \text{ or } Cu$) at 100 °C. After NO was introduced, several bands appeared at the surface. The bands at 1012 and 1187 cm^{-1} were assigned to bidentate NO_3^- and nitrosyl, respectively [38–40]. The bands at 1245 and 1613

cm^{-1} were due to the bridging NO_3^- , and the band at 1558 cm^{-1} derived from the bridging nitro [38,41,42]. With regard to CoO_x-CeO_2 (Fig. 4(a)), the intensity of the 1428 cm^{-1} band (NO_2^-) increased over time, which suggests that the NO species were consistently adsorbed onto the catalyst. With regard to FeO_x-CeO_2 (Fig. 4(b)), the intensity of the band at 1187 cm^{-1} (nitrosyl) initially increased and then decreased after 25 min. The intensities of the 1245, 1613 cm^{-1} (bridging NO_3^-), and 1558 cm^{-1} (bridging nitro) bands kept increasing after 10 min [38,43,44]. This suggests that the anionic nitrosyl gradually transformed into bridging NO_3^- and bridging nitro species over time. The $CuO-CeO_2$ catalyst (Fig. 4(c)) exhibited two additional bands, which were attributed to chelating nitro (1218 cm^{-1}) and monodentate NO_3^- (1503 cm^{-1}) [45]. The DRFTIR results allowed us to deduce that all the catalysts had a high capacity for NO adsorption because the intensities of the bands attributable to adsorbed NO all increased over time.

3.4.2. CO adsorption on MO_x-CeO_2 over time

The *in situ* DRFTIR spectra for CO adsorption onto the MO_x/CeO_2 ($M = Co, Fe, \text{ or } Cu$) catalysts are shown in Fig. 5. Bands appeared at 1032, 1052, 1215, 1295, 1390, 1466, 1535, and 1565 cm^{-1} after introducing CO for 1 min. The band at 1052 cm^{-1} was associated with CO_x , which originated from the reduction of cerium [46]. The bands at 1032 and 1466 cm^{-1} were attributed to monodentate CO_3^{2-} , whereas the band at 1295 cm^{-1} was related to CO_3^{2-} vibrations ($\nu_s(CO_3^{2-})$) [23,45,47–49]. The bands at 1390 and 1535 cm^{-1} were attributed to the symmetrical and asymmetrical stretching vibration modes of COO^- , respectively [43]. The broad band at approximately 1565 cm^{-1} was due to bidentate CO_3^{2-} , whereas the weak band at 1215 cm^{-1} was attributed to the formation of HCO_3^- [23,43]. With regard to the MO_x-CeO_2 catalysts ($M = Co, Fe, \text{ or } Cu$), the CO adsorption bands (e.g., CO_3^{2-} , HCO_3^- , COO^-) all appeared. However, we observed an additional band at 2100 cm^{-1} in $CuO-CeO_2$ (Fig. 5(d)). This band has been attributed to the linear Cu^+-CO species formed by CO molecules adsorbed at Cu^+ sites [23,50,51].

3.4.3. NO adsorption by CO-pretreated catalysts over time

As shown in Fig. 6, the MO_x-CeO_2 catalysts ($M = Co, Fe, \text{ or } Cu$) produced several bands related to CO_3^{2-} (1032, 1295, 1466, and 1565 cm^{-1}), HCO_3^- (1215 cm^{-1}), COO^- (1390 and

Fig. 4. *In situ* DRFTIR spectra showing adsorption of 1000 ppm of NO onto CoO_x-CeO_2 (a), FeO_x-CeO_2 (b), and $CuO-CeO_2$ (c) catalysts for various times at 100 °C.

Fig. 5. *In situ* DRFTIR results for adsorption of 1000 ppm of CO by fresh $\text{CoO}_x\text{-CeO}_2$ (a), $\text{FeO}_x\text{-CeO}_2$ (b), and CuO-CeO_2 (c) catalysts for various times at 100 °C.

Fig. 6. *In situ* DRFTIR spectra showing adsorption of 1000 ppm of NO by CO-pretreated catalysts comprising (a) $\text{CoO}_x\text{-CeO}_2$, (b) $\text{FeO}_x\text{-CeO}_2$, and (c) CuO-CeO_2 for various times at 100 °C.

1538 cm^{-1}), and ad-CO species (2100 cm^{-1}) following pre-treatment with CO for 30 min. When NO was introduced, the CO adsorption bands gradually disappeared, indicating the reaction between NO and CO. In particular, the characteristic band at 2100 cm^{-1} attributable to $\text{Cu}^+\text{-CO}$ species in CuO-CeO_2 rapidly vanished once NO was introduced, indicating high reactivity of the species in the CO-SCR reaction. Over time, only the adsorption bands attributable to NO were retained, i.e., NO_3^- (1012, 1245, 1280, and 1613 cm^{-1}), nitro species (1572 cm^{-1}), and nitrosyl (1187 cm^{-1}) [23,37].

3.4.4. CO adsorption by NO-pretreated catalysts over time

As shown in Fig. 7, bands attributable to bidentate NO_3^- (1012 cm^{-1}), bridging NO_3^- (1245, 1613 cm^{-1}), monodentate

NO_3^- (1280, 1503 cm^{-1}), and bridging nitro (1572 cm^{-1}) appeared following adsorption of NO for 30 min. These bands were retained after the introduction of CO, and no other bands representative of oxidized CO intermediates (e.g., CO_3^- and COO^-) were observed. This suggests that there was competitive adsorption of CO and NO in the catalysts. NO seemed to be adsorbed in preference to CO by the catalysts. Of the $\text{MO}_x\text{-CeO}_2$ catalysts ($M = \text{Co, Fe, or Cu}$), only CuO-CeO_2 exhibited CO-Cu^+ species at 2122 cm^{-1} after 10 min. This band gradually increased over time, suggesting that the Cu^+ retained CO adsorption in the catalyst during the CO-SCR reaction.

3.4.5. Co-adsorption of NO and CO over time

As shown in Fig. 8, we found that after exposure of the

Fig. 7. *In situ* DRFTIR spectra showing adsorption of 1000 ppm of CO by NO-pretreated $\text{CoO}_x\text{-CeO}_2$ (a), $\text{FeO}_x\text{-CeO}_2$ (b), and CuO-CeO_2 (c) catalysts for various times at 100 °C.

Fig. 8. *In situ* DRFTIR spectra showing co-adsorption of 1000 ppm of NO and 1000 ppm of CO by fresh CoO_x-CeO₂ (a), FeO_x-CeO₂ (b), and CuO-CeO₂ (c) catalysts for various times at 100 °C.

MO_x-CeO₂ catalysts (M = Co, Fe, or Cu) to CO and NO at 100 °C, the NiO-CeO₂, CoO_x-CeO₂, and FeO_x-CeO₂ catalysts preferentially adsorbed NO on their surfaces, forming NO₃⁻ (1012, 1245, 1280, and 1613 cm⁻¹), nitrosyl (1187 cm⁻¹), and nitro species (1215, 1572 cm⁻¹). In comparison, only the CuO-CeO₂ catalyst retained a distinct ad-CO band (2100 cm⁻¹). This result further confirms that Cu⁺ serves as an active site for CO adsorption, ensuring the CO-SCR reaction in the CuO-CeO₂ catalyst.

The DRFTIR results suggested that the CO-SCR reaction of the CoO_x-CeO₂ and FeO_x-CeO₂ catalysts proceeded according to an Eley-Rideal reaction mechanism (i.e., a reaction between absorbed NO and gaseous CO) due to the lack of CO adsorption by these catalysts. With regard to CuO-CeO₂, the presence of Cu⁺ species preserved the adsorption of CO. Therefore, this catalyst adopted a Langmuir-Hinshelwood SCR reaction mechanism. This explains why the CuO-CeO₂ catalyst exhibited the highest SCR activity in the SCR of NO by CO.

4. Conclusions

In the present study, we used an sc-H₂O hydrothermal route to synthesize MO_x-CeO₂ catalysts (M = Co, Fe, or Cu). This resulted in the formation of M_xCe_{1-x}O₂ solid solutions. H₂-TPR analyses revealed the following redox potential sequence: FeO_x-CeO₂ < CoO_x-CeO₂ < CuO-CeO₂. This was in accordance with the activity measurements for the catalysts with regard to the SCR of NO by CO. The DRFTIR results suggested that the MO_x-CeO₂ catalysts (M = Co or Fe) mainly followed an Eley-Rideal reaction mechanism for the CO-SCR of NO, whereas the CuO-CeO₂ catalyst adopted a Langmuir-Hinshelwood SCR reaction mechanism owing to the presence of Cu⁺ species, which ensured the effective adsorption of CO. This explains why CuO-CeO₂ exhibited the best catalytic activity with regard to the SCR of NO by CO.

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Graphical Abstract

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MO_x-CeO₂ (M = Co, or Fe) catalysts mainly follow an Eley-Rideal reaction mechanism for the selective catalytic reduction (SCR) of NO by CO, whereas CuO-CeO₂ adopts a Langmuir-Hinshelwood SCR reaction mechanism in which the Cu⁺ species ensure effective CO adsorption.

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超临界水热合成过渡金属改性铈基催化剂应用于CO-SCR脱硝研究

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摘要: 氮氧化物(NO_x)作为煤炭燃烧过程主要污染物之一, 可直接或间接引起如光化学烟雾、酸沉降、平流层臭氧损耗和全球气候变化等大气环境污染问题. NO_x的选择性催化还原技术(SCR)被认为是目前处理固定源NO_x的最有效方法之一. 由于燃煤工业锅炉烟气中还有1%~3%的CO, 远高于NO_x的0.02%~0.04%, 因此, 以CO为还原剂进行CO-SCR脱硝具有现实意义, 它可在反应过程中同时消除CO和NO两种有害气体, 但对催化剂的活性及抗毒性提出更高要求. CeO₂作为一种常用的

稀土材料, 因具有良好的储放氧能力而广泛应用于SCR反应中. 过渡金属改性可进一步改善 CeO_2 的物化性能, 从而可能达到CO-SCR的应用要求.

本文利用超临界水热技术合成了 $\text{MO}_x\text{-CeO}_2$ ($\text{M} = \text{Co}, \text{Fe}, \text{Cu}$)固溶体催化剂, 并利用X射线衍射(XRD), 氢气程序升温还原($\text{H}_2\text{-TPR}$), 傅里叶变换原位红外(DRFTIR)等探究了催化剂在CO-SCR反应中的催化活性与作用机制.

CO-SCR反应活性测试表明, CuO-CeO_2 催化剂活性明显优于 $\text{FeO}_x\text{-CeO}_2$ 和 $\text{CoO}_x\text{-CeO}_2$ 催化剂, 在126 °C NO去除率即可达到90%; 其 N_2 选择性也可在179 °C时达到90%. 为了进一步探究 $\text{MO}_x\text{-CeO}_2$ ($\text{M} = \text{Co}, \text{Fe}, \text{Cu}$)催化剂的CO-SCR反应途径, 本文随后进行了系列原位DRFTIR实验, 发现NO在三种催化剂表面均能被高效吸附, 其吸附态中间产物主要为双齿硝酸根, 桥式硝酸根, 桥式硝基和亚硝酰基等. 另外, 在 CuO-CeO_2 催化剂表面还存有螯合硝基和单齿硝酸根. CO在催化剂表面主要以 CO_x , 碳酸根和羧酸根等形式存在. 值得注意的是, 在 CuO-CeO_2 表面, CO因吸附于 Cu^+ 而形成 $\text{Cu}^+\text{-CO}$, 在2100 cm^{-1} 左右形成明显的特征峰. 当催化剂表面吸附CO至饱和后再通入NO发现, CO的吸附特征峰逐渐被NO的特征吸附峰取代; 而当NO被吸附至饱和后再通入CO, NO的特征峰则不出现明显变化. 这表明NO和CO在催化剂表面存在竞争吸附, NO可能优先于CO吸附在催化剂表面. 当NO和CO同时通入红外反应仓时发现, 在 $\text{CoO}_x\text{-CeO}_2$ 和 $\text{FeO}_x\text{-CeO}_2$ 催化剂表面只观察到NO的吸附峰, 而在 CuO-CeO_2 催化剂表面观察到 $\text{Cu}^+\text{-CO}$ 的特征峰, 说明在CO-SCR反应过程中, CO可以在 Cu^+ 表面被有效吸附, 其与吸附于 CeO_2 表面的NO物种反应生成 N_2 和 CO_2 , 遵循Langmuir-Hinshelwood反应机理. 而在 $\text{CoO}_x\text{-CeO}_2$ 和 $\text{FeO}_x\text{-CeO}_2$ 催化剂表面, 因NO的竞争吸附, 使得二者主要遵循Eley-Rideal反应机理.

关键词: 超临界水; 氮氧化物; CO; 选择催化还原; 傅里叶变换原位红外光谱; CeO_2

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