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Article

Effect of sulfur poisoning on $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxide catalyst for soot combustion

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ABSTRACT

CeO_2 , Co_3O_4 , and a series of $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides prepared by co-precipitation were exposed to SO_2 under an oxidizing environment at 400 °C. These fresh and SO_2 -poisoned samples were characterized by in situ diffuse reflectance infrared Fourier transform spectroscopy, X-ray diffraction, temperature-programmed desorption, and X-ray photoelectron spectroscopy. Sulfates were formed on the oxides, with more sulfates on CeO_2 than on Co_3O_4 . On the $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides, both cobalt sulphate and ceria sulfate were formed. Fresh and sulfated samples were tested for soot combustion in a NO/O_2 gas flow. The $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides showed better SO_2 tolerance and higher activity than CeO_2 but were more easily poisoned by SO_2 than Co_3O_4 .

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1. Introduction

A diesel particulate filter is applied for the removal of soot from diesel engine exhaust. The use of an oxidation catalyst coated on the filter is the preferred way to accelerate the combustion of accumulated soot and has been widely studied. Various soot oxidation catalysts have been developed, and many metal oxides can lower the soot oxidation temperature [1–5]. Ceria-supported cobalt oxides prepared by different routes exhibited good performance for soot combustion [6–12]. Harrison et al. [6] deduced that the high catalytic activity of Co/CeO_2 in soot combustion was due to the presence of cobalt in the catalyst as Co_3O_4 and the redox properties of CeO_2 . A spillover mechanism at the cobalt oxide-ceria interface was postulated to drive the soot oxidation. Methane oxidation experiments are sometimes performed as a test of soot oxidation

[13]. $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides prepared by a co-precipitation method showed a superior activity for methane oxidation and CO oxidation and have good resistance to water vapor poisoning [13,14].

From a practical point of view, studying the effect of SO_2 on $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides is of importance because SO_2 is present in the exhaust gases. In the present study, a series of $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxide catalysts were prepared by the co-precipitation method. The sulfation of the $\text{Co}_3\text{O}_4/\text{CeO}_2$ catalysts was investigated using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The soot oxidation activity of the fresh and SO_2 -poisoned $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides was investigated and compared using temperature-programmed oxidation (TPO).

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2. Experimental

2.1. Catalyst preparation

$\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides with increasing Co_3O_4 loading corresponding to Co/Ce atomic ratios of 0.05–5 (denoted by $\text{Co}_{0.05}\text{Ce}$, $\text{Co}_{0.2}\text{Ce}$, $\text{Co}_{1.0}\text{Ce}$, $\text{Co}_{2.0}\text{Ce}$, and $\text{Co}_{5.0}\text{Ce}$), CeO_2 , and Co_3O_4 were prepared by a co-precipitation method with a K_2CO_3 solution (15 wt%). In a typical preparation, K_2CO_3 solution was added dropwise to an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in appropriate amounts until the pH was 9.10. The mixture solution was stirred for 1 h and was aged at room temperature for 3 h. Then the resulting precipitate was filtered and washed with distilled water until the filtrate pH was neutral. The precipitate was dried overnight at 110 °C and calcined for 2 h at 400 °C in air.

To sulfate the catalysts, 40–60 mesh catalysts were treated with 300 ppm SO_2 and 10% O_2 in N_2 at a flow rate of 400 ml/min at 400 °C for different times. The SO_2 -poisoned catalysts were denoted according to the treatment time, for instance, $\text{Co}_{1.0}\text{Ce-S-10h}$ was the $\text{Co}_{1.0}\text{Ce}$ catalyst sulfated at 400 °C for 10 h.

2.2. Catalytic activity measurements

The soot used in this work was Printex-U (Degussa), which is a model soot reported elsewhere. The catalyst-soot mixture (9:1 w/w) for the TPO reaction was obtained by careful grinding in an agate mortar for 10 min (tight contact). It is known that the contact between the soot and catalyst influences the oxidation reaction significantly [3,15]. Although the soot/catalyst contact obtained by the current mixing procedure did not reflect the actual contact conditions in a catalytic soot trap, nevertheless it permitted reproducible results under the present experimental conditions [16,17]. A catalyst-soot mixture diluted with 1.00 g quartz pellets was carefully mixed and put into the quartz tube reactor (internal diameter 6 mm). The TPO test was carried out by heating the soot/catalyst mixture from 200 to 600 °C (heating rate 2 °C/min) under a total flow rate of 100 ml/min (NO 1000 ppm, O_2 5%, Ar as balance). CO_2 analysis was performed by GC/TCD (Porapak Q, Agilent) at intervals of

5 min.

2.3. Catalyst characterization

The samples were characterized by XRD using a computerized Rigaku D/max-RB diffractometer (Japan, $\text{Cu K}\alpha$ radiation). Data were recorded in the 2θ range of 10°–90° with an angle step size of 0.02° and a scanning speed of 4°/min.

XPS analysis was performed with an EASY ESCA instrument. The spectra were excited by an Al $K\alpha$ source (1486.6 eV), and the analyzer was operated in the constant analyzer energy (CAE) mode. Survey spectra were measured at 50 eV pass energy. Charging of the samples was corrected for by referencing all the energy to the C 1s peak energy (set at 285.0 eV).

TPD was performed in a system equipped with a quadrupole mass spectrometer (Hiden HPR20). In the SO_2 -TPD, the SO_2 -poisoned sample was placed in a quartz tube reactor (internal diameter 4 mm). Pure He was used as the carrier, and the total flow of carrier was held at 30 ml/min with the temperature increase rate of 30 °C/min. All the samples used in the TPD experiments were the same weight of 300 mg and the same size of 40–60 mesh.

DRIFTS spectra were recorded in situ with a Nexus 670 FT-IR spectrometer (Thermo Nicolet) equipped with a diffuse reflection chamber and a high sensitivity MCT/A detector cooled by liquid nitrogen. The catalysts for the DRIFTS study was finely ground and placed in a ceramic crucible. All spectra were measured with a resolution of 4 cm^{-1} and with an accumulation of 100 scans. Sulfate accumulation on test catalysts was investigated by DRIFTS in a flow of SO_2 300 ppm, O_2 20%, and N_2 as balance for 60 min at 400 °C.

3. Results and discussion

3.1. Activity test

The TPO results of soot combustion in a NO/O_2 mixture over the various $\text{Co}_3\text{O}_4/\text{CeO}_2$ oxides, pure CeO_2 , and Co_3O_4 are shown in Fig. 1(a). Clearly, the presence of cobalt greatly improved the soot oxidation activity of CeO_2 even at as low a content as Co/Ce = 0.05. The catalytic activity for soot combustion showed

Fig. 1. TPO profiles of soot-catalyst mixtures (soot:catalyst = 1:9 by weight). (a) Fresh catalysts; (b) 6 h SO_2 -poisoned catalysts; (c) Various SO_2 -poisoned catalysts. Reactant gas: 1000 ppm NO + 5% O_2 in Ar. Heating rate: 2 °C/min. SO_2 poison conditions: 300 ppm SO_2 and 5% O_2 in N_2 at 400 °C.

little dependence on the Co/Ce ratio of the $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxide when the Co/Ce atomic ratio was higher than 0.2. $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides with Co/Ce atomic ratios ranging from 0.2 to 5.0 showed a similar activity with a maximum in the temperature range 330–350 °C. In the studies of Dhakad et al. [7] and Liu et al. [8], Co_3O_4 - CeO_2 oxides or CeO_2 supported Co showed significantly improvement for soot combustion compared to CeO_2 and Co_3O_4 . There was a synergistic effect between ceria and cobalt. For studying the effect of SO_2 on the activity of soot oxidation over $\text{Co}_3\text{O}_4/\text{CeO}_2$, $\text{Co}_0.2\text{Ce}$, $\text{Co}_{1.0}\text{Ce}$, and $\text{Co}_{5.0}\text{Ce}$ were treated in a flow of a $\text{SO}_2 + \text{O}_2$ mixture at 400 °C for 6 h. Then the TPO experiments were carried out. As seen in Fig. 1(b), the treatment by SO_2 caused some loss of activity for the tested samples. The $\text{Co}_{1.0}\text{Ce}$ catalyst displayed the best SO_2 resistance among the three tested samples. Based on these results, the $\text{Co}_{1.0}\text{Ce}$ catalyst was selected for further studies.

Figure 1(c) shows the TPO profiles of the $\text{Co}_{1.0}\text{Ce}$ catalysts with different SO_2 exposure time, the TPO profile for CeO_2 after sulfation for 20 h and for Co_3O_4 after sulfation for 40 h. The activity of the $\text{Co}_{1.0}\text{Ce}$ catalyst decreased with increasing sulfur poisoning time. With increasing sulfur poisoning time, soot oxidation by the $\text{Co}_{1.0}\text{Ce}$ catalyst started at a slower rate, and it was completed at a higher temperature. The TPO profile of $\text{Co}_{1.0}\text{Ce-S-40h}$ consisted of a double peak, which showed better catalytic activity than CeO_2 sulfated for 20 h. Co_3O_4 showed the best sulfur resistance in soot oxidation under tight contact.

3.2. Characterization analysis

Figure 2 shows the XRD patterns of the CeO_2 , Co_3O_4 , and $\text{Co}_{1.0}\text{Ce}$ catalysts (fresh, 15 h sulfated, and 40 h sulfated). All the reflections of pure cobalt oxide and pure cerium oxide were assignable to the cobalt spinel structure (JCPDS 80-1541) and fluorite oxide structure (JCPDS 34-0394), respectively. There was no other phase on the $\text{Ce}_{1.0}\text{Co}$ catalysts except for these two phases. The broad Co_3O_4 peaks observed in the fresh $\text{Co}_{1.0}\text{Ce}$ indicated that the Co_3O_4 was well dispersed on the CeO_2 . The XRD patterns of the sulfated $\text{Ce}_{1.0}\text{Co}$ catalysts were almost the same as the fresh sample, which indicated that no crystalline sulfate species was formed on the $\text{Ce}_{1.0}\text{Co}$ catalysts

Fig. 2. XRD patterns of CeO_2 , $\text{Co}_{1.0}\text{Ce}$, $\text{Co}_{1.0}\text{Ce-S-15h}$, $\text{Co}_{1.0}\text{Ce-S-40h}$, and Co_3O_4 .

Fig. 3. SO_2 TPD results using a He carrier gas for the various samples.

from the sulfation.

The SO_2 -TPD results of the sulfated samples are illustrated in Fig. 3. These showed that the decomposition of the sulfate species to SO_2 was at 800 °C for $\text{CeO}_2\text{-S-20h}$ and at 840 °C for $\text{Co}_3\text{O}_4\text{-S-40h}$. The TPD curves of $\text{Ce}_{1.0}\text{Co-S-15h}$ and $\text{Ce}_{1.0}\text{Co-S-40h}$ showed two SO_2 desorption peaks: a large low-temperature peak at 845 °C and a minor high-temperature peak at 890 °C. In addition, the low-temperature desorption peaks increased significantly with increased SO_2 treatment time, while the high-temperature peaks were independent of SO_2 treatment time. More interestingly, the $\text{Ce}_{1.0}\text{Co-S-10h}$ sample only showed the high-temperature peak at around 890 °C. It has been reported that sulfation of the CeO_2 resulted in both surface and bulk sulfates [18,19]. After exposure to 1% SO_2 in excess O_2 at 400 °C, the TPD in He of Pd/CeO_2 gave a SO_2 peak at 750 °C assigned to Ce^{4+} sulfate, and the peak of the decomposition of Ce^{3+} sulfate to SO_2 was at a higher temperature of 850 °C [18]. Only one peak of SO_2 decomposition on CeO_2 was observed at 800 °C here. In this study, the exposure of the samples to SO_2 in excess O_2 at 400 °C was carried out for a long time (up to 40 h). It has been shown that the stable sulfate formed at 400 °C in the presence of excess O_2 is $\text{Ce}_2(\text{SO}_4)_3$ and not $\text{Ce}(\text{SO}_4)_2$ [18,19]. This suggested that the high intensity peak at 840 °C observed for $\text{Co}_{1.0}\text{Ce-S-15h}$ and $\text{Co}_{1.0}\text{Ce-S-40h}$ should be associated with Ce^{3+} sulfate. The small sulfate decomposition peaks at 890 °C observed in the $\text{Co}_{1.0}\text{Ce-S-10h}$, $\text{Co}_{1.0}\text{Ce-S-15h}$, and $\text{Co}_{1.0}\text{Ce-S-40h}$ were associated with the same sulfate species, and the amount of SO_2 from the decomposition at 890 °C was the same for $\text{Co}_{1.0}\text{Ce-S-15h}$ and $\text{Co}_{1.0}\text{Ce-S-40h}$.

The interaction of SO_2 with the chosen $\text{Co}_{1.0}\text{Ce}$ catalyst was also studied by XPS. In Fig. 4, the experimental and fitted $\text{Ce } 3d$ spectra of fresh $\text{Ce}_{1.0}\text{Co}$ and $\text{Co}_{1.0}\text{Ce-S-40h}$ are shown. The spectra in the $\text{Ce } 3d$ region were fitted with eight peaks corresponding to four pairs of spin-orbit doublets [19]. The labeling of the peaks followed the convention adopted by Teterin et al. [20]. According to the literature [13,19,20], three pairs of peaks (V , U ; V'' , U'' ; V''' , U''') are the characteristic of the Ce^{4+} oxidation state while the couple (V' , U') corresponds to Ce^{3+} ions. An obvious increase in the intensity of the couple (V' , U') peaks was observed in the $\text{Ce } 3d$ spectra of $\text{Co}_{1.0}\text{Ce-S-40h}$, which suggested that Ce^{3+} species on the $\text{Co}_{1.0}\text{Ce}$ catalyst increased

Fig. 4. Experimental and fitted Ce 3d XPS spectra for Co1.0Ce (a) and Co1.0Ce-S-40h (b).

during the reaction with SO₂ in an excess of O₂. This indicated that during the sulfation of Co1.0Ce at 400 °C, Ce⁴⁺ ions were gradually reduced to Ce³⁺. This result was in accordance with those reported by Smirnov et al. [19]. The atomic ratio Ce³⁺/(Ce⁴⁺+Ce³⁺) was estimated from the ratio of the intensity of V' and U' components to the total intensity of the entire Ce 3d curve [19]. The calculation showed that the fraction of Ce³⁺ ions in the fresh Co1.0Ce and Co1.0Ce-S-40h was 14% and

22%, respectively. This suggested 8% increase in Ce³⁺ species of Co1.0Ce related to the 40 h exposure to SO₂ in excess O₂.

Figure 5 illustrates the experimental XPS spectra of the Co 2p_{3/2}, O 1s, and S 2p regions for fresh Co1.0Ce and Co1.0Ce-S-40h. The Co 2p_{3/2} peak binding energy (BE) for Co1.0Ce appeared at 781.2 eV, in agreement with the reference data [13,14,21]. There was no change in the BE for Co 2p_{3/2} of Co1.0Ce-S-40h, which was observed at 781.1 eV. A high intensity S 2p feature appeared from Co1.0Ce-S-40h at 169.2 eV and can be assigned to cerium sulfate species [19]. The O 1s feature recorded from fresh Ce1.0Co was at 529.6 eV while that from Co1.0Ce-S-40h was sifted to a higher BE (~532 eV) and had increased intensity. The oxygen in the large amount of sulfate species caused the shift and increased intensity of the O 1s BE and peak.

Figure 6 shows the DRIFTS spectra with time of CeO₂, Co₃O₄, and Co1.0Ce after exposure to a flow of SO₂+O₂ at 400 °C. Several bands in the 1400–900 cm⁻¹ region appeared after the exposure to the SO₂+O₂ gas. The broad band at 1130 cm⁻¹ with the highest intensity was due to the sulfates in the bulk [22,23]. The small bands at 1334 cm⁻¹ can be assigned to surface sulfate. The species responsible for the peak at 1001 cm⁻¹ (970 cm⁻¹ in the spectrum from Co₃O₄) can be assigned to sulfites [22].

From the comparison of the changes of the DRIFTS spectra of CeO₂, Co₃O₄, and Co1.0Ce with time, it was deduced that both cobalt sulfate and ceria sulfate were formed during the exposure of the catalysts to the SO₂+O₂ flow. The spectra recorded from CeO₂ with time were essentially identical (Fig. 6(a)). The shift of the band at 1100 cm⁻¹ to higher vibration was caused by the accumulation of sulfate species. This strong and broad band at 1138 cm⁻¹ was due to the formation of bulk Ce(SO₄)₂ [23,24]. The IR bands from Co1.0Ce are shown in Fig. 6(b). Surface and bulk sulfates species, which were attributed to

Fig. 5. Experimental and fitted XPS spectra for fresh Co1.0Ce and Co1.0Ce-S-40h. (a) Co 2p; (b) S 2p; (c) O 1s.

Fig. 6. DRIFTS spectra with time of the different catalysts at 400 °C in a flow of $\text{SO}_2 + \text{O}_2$. (a) CeO_2 ; (b) Co1.0Ce ; (c) Co_3O_4 .

1400–1340 and 1200–1100 cm^{-1} range, were formed and increased with increasing sulfur exposure time [21].

3.3. Discussion

Soot catalytic oxidation has different mechanisms. The mechanism that dominates depends on the contact between the catalyst and soot. The preparation procedure of the catalyst and soot mixture in this study produced the contact that is essentially “tight contact” [1–3]. In the NO_x -assisted soot oxidation reaction over CeO_2 , ‘active oxygen’ generated from both nitrate and surface oxygen decomposition plays an important role in the acceleration of soot oxidation [4]. A redox mechanism assisted by oxygen spillover on CeO_2 occurs in the Co/CeO_2 catalyzed reaction of soot in a NO/O_2 mixture [6]. In the literature [4,6,7,8,25], a redox mechanism on Co sites and a spillover mechanism from Ce sites were proposed for the activity of $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides in soot oxidation. The redox properties and the active oxygen generated from surface nitrate decomposition were proposed to be important factors for soot combustion in a NO/O_2 mixture. The redox mechanism would be the dominant mechanism for soot oxidation activity in the contact type used in this work. The slight difference in soot combustion activity between the $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides with different Co/Ce ratios ($\text{Co}/\text{Ce} > 0.2$) can be understood with this mechanism.

Sulfur exposure significantly decreased the activity of CeO_2 for soot combustion. The temperature of the TPO maximum for fresh CeO_2 was 410 °C and for CeO_2 -S-20h was 525 °C. Peralta et al. [26] reported that the temperature of the TPO maximum increased from 523 to 558 °C in loose contact after 31 h SO_2 treatment. This suggested that the effect of sulfur exposure on catalytic activity was more significant for tight contact than for

loose contact, which suggested that the sulfur exposure mainly influenced the redox property of CeO_2 , which was important for soot combustion in tight contact.

A significant sulfur tolerance was observed with $\text{Co}_3\text{O}_4/\text{CeO}_2$ compared to CeO_2 . The TPO maximum for Co1.0Ce was increased from 340 to 370 °C. A continuous decrease in activity of Co1.0Ce was observed with the increase in exposure time. Sulfate accumulation on Co1.0Ce increased with increasing SO_2 treatment time according to the SO_2 -TPD profiles (Fig. 4). The FTIR spectra suggested that both cerium sulfate (Ce^{3+} and Ce^{4+}) and cobalt sulfate species were formed on Co1.0Ce after exposure to the $\text{SO}_2 + \text{O}_2$ gas flow at 400 °C. For CeO_2 , bulk sulfate $\text{Ce}(\text{SO}_4)_2$ was largely formed by exposure to $\text{SO}_2 + \text{O}_2$ at 400 °C [19,24]. $\text{Ce}_2(\text{SO}_4)_3$ was the only stable sulfate under the current sulfur exposure condition [18]. The formation of sulfate species on ceria was generally accompanied by the reduction of Ce^{4+} to Ce^{3+} [19]. The sulfation of $\text{Co}_3\text{O}_4/\text{CeO}_2$ (Co1.0Ce) showed similar results to that of CeO_2 . A significant increase of Ce^{3+} in $\text{Co}_3\text{O}_4/\text{CeO}_2$ was shown by the XPS results. A long exposure time to $\text{SO}_2 + \text{O}_2$ showed no effect on the electronic state of the cobalt according to the XPS results. Liotta et al. [21] also found that the Co 2p spectrum did not change upon sulfur poisoning when they studied the SO_2 effect on $\text{Pd}/\text{Co}_3\text{O}_4$ catalysts for CH_4 oxidation. This suggested that $\text{Co}_3\text{O}_4 \cdot \text{SO}_3$ was the dominant sulfate formed on Co_3O_4 [21]. The double peak in the TPO profile of Co1.0Ce -S-40h can be attributed to the activity of Co_3O_4 in the catalyst.

4. Conclusions

The exposure of CeO_2 , Co_3O_4 , and $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides to SO_2 under oxidizing conditions at 400 °C resulted in the formation of sulfate. The decomposition of cerium sulfate

Graphical Abstract

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Effect of sulfur poisoning on $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxide catalyst for soot combustion

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$\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides showed better SO_2 tolerance and higher activity than CeO_2 but was more easily poisoned by SO_2 than Co_3O_4 during soot combustion in NO/O_2 .

occurred at a lower temperature than cobalt sulfate. Both cobalt sulfate and ceria sulfate were formed on $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides during SO_2 exposure. Ce^{4+} was gradually reduced to Ce^{3+} during the sulfation process. Bulk sulfate was formed on CeO_2 , and the cobalt sulfate mainly existed as $\text{Co}_3\text{O}_4\cdot\text{SO}_3$.

A series of $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides prepared by co-precipitation showed better catalytic activity for soot combustion in tight contact than CeO_2 . Sulfur poisoning resulted in a decrease in activity of the $\text{Co}_3\text{O}_4/\text{CeO}_2$ composite oxides, CeO_2 , and Co_3O_4 . The sulfur tolerance of $\text{Co}_3\text{O}_4/\text{CeO}_2$ was higher than CeO_2 but lower than Co_3O_4 .

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硫中毒对 $\text{Co}_3\text{O}_4/\text{CeO}_2$ 复合氧化物上炭黑催化燃烧的影响石晓燕^a, 余运波^a, 薛莉^b, 贺泓^{a,*}^a中国科学院生态环境研究中心, 北京100085^b山东理工大学化学工程学院, 山东淄博255049

摘要: 采用共沉淀法制备了 CeO_2 , Co_3O_4 和一系列 $\text{Co}_3\text{O}_4/\text{CeO}_2$ 复合氧化物催化剂, 在400 °C下含 SO_2 的氧化气氛中对催化剂进行了

硫中毒处理, 通过原位红外光谱、X射线衍射、程序升温脱附和X射线光电子能谱对新鲜和硫中毒的样品进行了表征. 结果表明, 所有测试的硫中毒样品上均形成了硫酸盐, CeO_2 上累积的硫酸盐明显比 Co_3O_4 上的多, $\text{Co}_3\text{O}_4/\text{CeO}_2$ 复合氧化物在硫中毒过程中形成了硫酸钴和硫酸铈. 对新鲜和硫化样品在 NO/O_2 气氛下进行了催化炭黑燃烧实验, 发现 $\text{Co}_3\text{O}_4/\text{CeO}_2$ 复合氧化物的活性和抗硫性能优于 CeO_2 , 但抗硫性能低于 Co_3O_4 .

关键词: 炭黑氧化; 氧化钴; 氧化铈; 复合氧化物; 硫中毒

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