CeO₂-Co₃O₄ Catalysts for CO Oxidation

Xu Xiuyan (许秀艳), Li Jinjun (李进军), Hao Zhengping (郝郑平)*

(Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China)

Received 14 April 2005; revised 13 July 2005

Abstract: CeO₂-Co₃O₄ catalysts for low-temperature CO oxidation were prepared by a co-precipitation method. In combination with the characterization methods of N₂ adsorption/desorption, XRD, temperature-programmed reduction (TPR), and FT-IR, the influence of the cerium content on the catalytic performance of CeO₂-Co₃O₄ was investigated. The results indicate that the prepared CeO₂-Co₃O₄ catalysts exhibit a better activity than that of pure CeO₂ or pure Co₃O₄. The catalyst with the Ce/Co atomic ratio 1:16 exhibits the best activity, which converts 77% of CO at room temperature and completely oxidizes CO at 45 °C.

Key words: CO oxidation; CeO₂; Co₃O₄; CeO₂-Co₃O₄ catalyst; rare earths

CLC number: O643.3 **Document code:** A **Article ID:** 1002-0721(2006)02-0172-05

Cobalt oxides are usually used as catalysts in oxidation reactions. Cobalt oxides show very high CO oxidation activity at ambient temperature^[1]. In addition, it is only the preoxidised cobalt oxide catalyst that shows activity at low temperature^[2].

Of late, ceria-based materials have been receiving tremendous attention because of their diverse application in catalysis and other fields. Potential uses of CeO₂ for removal of soot from diesel engine exhausts, for removal of the organics from wastewaters and as an additive for combustion process have been described^[3,4]. The successful utilization of ceria in pollution abatement and other technologies is mainly on account of its elevated oxygen transport capacity coupled with the ability to shift easily between reduced and oxidized states (Ce³⁺ ↔ Ce⁴⁺). Furthermore, it is suggested that the formation of mixed oxides of ceria with other cations such as Zr⁴⁺, Al³⁺, and La³⁺ enhances the thermal stability, redox and oxygen storage properties of ceria^[5,6].

Following these considerations, we studied low-temperature CO oxidation on mixed oxides of CeO₂-Co₃O₄. In combination with the characterization methods of N₂ adsorption/desorption, XRD, TPR, and FT-IR, the influence of cerium content on the catalytic performance of CeO₂-Co₃O₄ catalysts was investigated.

1 Experimental

1.1 Catalyst preparation

CeO₂-Co₃O₄ catalysts were prepared by co-precipitation. A mixed aqueous solution of Ce(NO₃)₃·6H₂O and Co(NO₃)₂·6H₂O was gradually added into Na₂CO₃ solution with continuous stirring. After 2 h, the resulting precipitate was filtered and washed by deionized water, after which the solids were dried at 70 °C, and finally calcined at 500 °C for 3 h. The CeO₂-Co₃O₄ samples were named as Ce_xCo_y (*x* and *y* being the

* Corresponding author (E-mail: zpinghao@mail.rcees.ac.cn)

Foundation item: Project supported by the National Basic Research Program of China (2004CB719500) and the Key Project of Knowledge Innovation of Chinese Academy of Sciences (KZCX3-SW-430)

Biography: Xu Xiuyan (1977–), Female, Doctoral candidate

atomic ratio between cerium and cobalt). The pure CeO₂ and Co₃O₄ catalysts were also prepared by the similar procedures.

1.2 Catalyst characterization

BET surface areas of the samples were measured by nitrogen adsorption/desorption at liquid nitrogen temperature, using a gas adsorption analyzer NOVA 1200. Thermo gravimetric and differential scanning calorimetric analysis (TG-DSC) of the samples was carried out using a Setaram Labsys-16 thermal analyzer in the range of 15 ~ 800 °C, in air. The heating rate was maintained at 10 °C · min⁻¹. XRD analysis was performed with a D5005D X-ray diffractometer. Diffraction patterns were recorded with Cu Kα radiation (40 mA, 40 kV) and a position-sensitive detector using a step size of 0.04° and a step time of 0.5 s. TPR tests were carried out in a continuous flow quartz reactor, which was connected with a TCD detector. In each test, 0.05 g of the catalyst was used, and the heating rate was 10 °C · min⁻¹. FT-IR spectra were obtained with a spectral resolution of 4 cm⁻¹ by using a Bruker TENSOR 27 FT-IR spectrometer equipped with an LN-MCT Mid [Internal] detector. All the samples inside the IR cell were initially pretreated in vacuum at 200 °C for 30 min and then cooled down to room temperature. The spectrum of the pretreated sample was used as a background from which the adsorbed spectrum was subtracted.

1.3 Catalytic activity

The catalytic activity was investigated by using a fixed-bed continuous flow reactor, and the catalyst bed temperature was measured by a K-type thermocouple. A sample (400 mg, 60 ~ 80 mesh) was placed in a quartz tube reactor with an inner diameter of 6 mm. A mixture of CO (5%, volume fraction) and air was admitted at a flow rate of 66.7 ml · min⁻¹, resulting in a space velocity of 10,000 ml · h⁻¹ · g_{cat}⁻¹. The exit gases from the reactor were analyzed by on-line gas chromatography (SP-2100), equipped with a hydrogen flame ionization detector, connected with a carbon sieve column.

2 Results and Discussion

The TG-DSC curves of the Ce₁Co₁₆ precursor before calcination are shown in Fig.1. The TG curve exhibits a large weight loss of about 25% between 80 and 250 °C, which accompanies a distinct endothermic peak at 160 °C in the DSC curve, corresponding to the dehydration of the surface adsorbed water and the transformation of the hydroxide to an oxide. On the other

hand, an obvious exothermic event at about 250 °C corresponds to the decomposition of nitrate species possibly retained in the solids washed and dried at 70 °C^[7]. No further weight loss is observed after 500 °C. Thus we selected a calcination temperature of 500 °C.

Reaction experiments for CO oxidation on the catalysts prepared with different Ce/Co atomic ratios were carried out. Fig. 2 shows the conversion of CO as a function of temperature on the tested catalysts. The activity of either CeO₂ or Co₃O₄ for CO oxidation is very low at room temperature, but the activities of CeO₂-Co₃O₄ catalysts are much higher than that of CeO₂ or Co₃O₄. The increase of CeO₂-Co₃O₄ catalytic activities may be caused by the strong interaction between CeO₂ and Co₃O₄. The catalytic activity of the CeO₂-Co₃O₄ depends on the Ce/Co atomic ratio. Among these catalysts, Ce₁Co₁₆ exhibits the best activity, which converts 77% of CO at room temperature and completely oxidizes CO at 45 °C.

In order to find the relation between the Ce/Co atomic ratio and the catalytic activity, several characterization methods were employed. The BET surface areas of CeO₂-Co₃O₄ catalysts were measured and the results were summarized in Table 1. Pure Co₃O₄ shows

Fig.1 TG-DSC curves of Ce₁Co₁₆ precursor

Fig.2 Catalytic activity of all catalysts for CO conversion
(1) CeO₂ denoted by ●; (2) Co₃O₄ denoted by ■;
(3) Ce₁Co₂₈ denoted by ◆; (4) Ce₁Co₈ denoted by ▲;
(5) Ce₁Co₁₆ denoted by ▼

Table 1 BET surface areas of catalysts

Samples	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$
CeO ₂	126
Ce ₁ Co ₈	140
Ce ₁ Co ₁₆	148
Ce ₁ Co ₂₈	141
Co ₃ O ₄	25

a very low surface area, while pure CeO₂ gives a relatively higher surface area. It should be noted that CeO₂-Co₃O₄ catalysts (i. e., Ce₁Co₈, Ce₁Co₁₆ and Ce₁Co₂₈) have even larger surface areas than pure CeO₂. Ce₁Co₁₆ that shows the best activity has the largest surface area. These results indicate that large surface areas have a positive effect on catalytic activity.

The XRD patterns of Co₃O₄, CeO₂, and various CeO₂-Co₃O₄ catalysts are shown in Fig.3. The diffractogram of pure CeO₂ presents a very strong peak at $2\theta = 28.5^\circ$ and other weak peaks characteristic of fluorite CeO₂^[8]. However, ceria peaks are not observed in the XRD patterns of the CeO₂-Co₃O₄ catalysts, although several obvious peaks characteristic of spinel Co₃O₄ could be detected, which may be on account of the formation of Ce-Co-O solid solution or highly dispersed CeO₂ on the surface of Co₃O₄ support^[9]. Compared to the pure Co₃O₄, the characteristic spinel Co₃O₄ peaks of the CeO₂-Co₃O₄ catalysts become wider. According to Scherer equation^[10], the crystallite size of pure Co₃O₄ is calculated as being 26.5 nm, while the Co₃O₄ crystallite sizes in Ce₁Co₈, Ce₁Co₁₆ and Ce₁Co₂₈ are 7.2, 7.8 and 8.0 nm, respectively. These results indicate that the addition of cerium oxide greatly decreases the crystallite size of Co₃O₄, therefore CeO₂-Co₃O₄ catalysts exhibit better catalytic activity than pure Co₃O₄^[11].

Fig.3 X-ray diffraction patterns for Co₃O₄, CeO₂ and various CeO₂-Co₃O₄ catalysts

Fig. 4 displays the H₂-TPR profiles of Co₃O₄, CeO₂, and various CeO₂-Co₃O₄ catalysts. The profile of pure CeO₂ shows a single weak peak at 380 °C, which is because of the reduction of the CeO₂ surface oxygen^[12], while a pure Co₃O₄ crystallite undergoes reduction at about 390 °C. Compared to that of pure Co₃O₄ in the case of CeO₂-Co₃O₄ catalysts with different Ce/Co atomic ratio, the reduction peaks are all shifted to lower temperatures. Among these catalysts, Ce₁Co₁₆ displays the lowest Co₃O₄ crystallite reduction temperature in the H₂-TPR profiles, which is in good agreement with its being the best catalytic activity.

In order to thoroughly understand the reason behind the activity enhancement of CeO₂-Co₃O₄ catalysts, CO adsorption spectra on the Ce₁Co₁₆ and the pure Co₃O₄ both in the absence and presence of air were investigated by the FT-IR technique. Fig. 5 shows CO adsorption FT-IR spectra of Ce₁Co₁₆ and Co₃O₄ in the absence of air. Adsorption of CO (Equilibrium pressure at 34.8 kPa) on pretreated Ce₁Co₁₆ and Co₃O₄ leads to the appearance of bands at 2168 and 2120 cm⁻¹. With high CO concentration, the bands at 2168 and 2120 cm⁻¹ on the Ce₁Co₁₆ and the Co₃O₄ are so consistent with the bands indicative of CO in the gas phase (this spectrum obtained by gold mirror

Fig.4 TPR profiles for Co₃O₄, CeO₂ and various CeO₂-Co₃O₄ catalysts **Fig.5** CO adsorption FT-IR spectra of Ce₁Co₁₆ and Co₃O₄ at 34.8 kPa after 30 min

is not shown) that they are mainly ascribed to CO adsorption peak in the gas phase. A weak band near 2305 cm⁻¹ is observed during the CO adsorption on the Ce₁Co₁₆ and the Co₃O₄, but disappears upon vacuum degassing. This band can readily be assigned to the combination mode of the cobalt-carbon vibration with the intense CO mode polarized by cobalt ions^[13]. In the case of Ce₁Co₁₆, it should be noted that CO₂ binds to Ce₁Co₁₆ at 2341 cm⁻¹ and the adsorption peak shape is rather sharp. In addition, bicarbonate species are also observed at 1661, 1414 and 1216 cm⁻¹, which are believed to be the reaction intermediate^[14,15]. However, for Co₃O₄, the very weak CO₂ adsorption band indicates the presence of a negligible amount of CO₂, and no bicarbonates could be detected. Analysis of the FT-IR results show that CeO₂ surface oxygen could be responsible for the formation of bicarbonates and CO₂ in the "CO-only" system, and is responsible for better activity of Ce₁Co₁₆ than that of Co₃O₄.

For comparison, CO adsorption FT-IR spectra of Ce₁Co₁₆ and Co₃O₄ in the presence of air are shown in Fig.6. CO adsorption bands at 2173 and 2121 cm⁻¹ on the Co₃O₄ are observed. The band of 2173 cm⁻¹ lies at a higher frequency than that of gaseous CO, which suggests that the CO molecule is absorbed in a relatively high oxidation state cation through donating its electrons in this σ -type coordination bond^[16]. Therefore this band can be assigned to the CO adsorption on the coordinative unsaturated Co³⁺ sites. At the same time, a band centers at 2121 cm⁻¹, which can be ascribed to the CO adsorbed on Co²⁺ sites^[17]. For the Ce₁Co₁₆, the addition of the cerium element leads to the different coordination of the cobalt atoms, so the CO adsorption band shifts a little and centers at 2184 and 2105 cm⁻¹. In the presence of air, more reaction intermediates are produced on both Ce₁Co₁₆ and Co₃O₄,

Fig. 6 CO reaction FT-IR spectra of Ce₁Co₁₆ and Co₃O₄ after 30 min (5%CO, balance air, flow rate = 10 ml·min⁻¹)

all of which could be proved by the bands at 1647, 1559, 1428 and 1360 cm⁻¹ for Co₃O₄ and at 1643, 1537, 1496 and 1365 cm⁻¹ for Ce₁Co₁₆^[14,15]. Interestingly, for both Ce₁Co₁₆ and Co₃O₄, although large amount of CO₂ is produced during the CO reaction according to activity data, no obvious bands pertaining to CO₂ are observed in the spectra. These results indicate that the interaction between the CO₂ and the catalyst surface is so weak that CO₂ desorb easily from the catalyst surface. This also contributes to the good activity of the catalysts at room temperature.

3 Conclusion

CeO₂-Co₃O₄ catalysts show a better catalytic activity in the CO oxidation reaction when compared to pure Co₃O₄. The phase cooperation between CeO₂ and Co₃O₄ is responsible for the activity enhancement. The addition of a small amount of cerium oxide greatly decreases the crystallite size of Co₃O₄. At the same time, a larger surface area is generated. FT-IR results further show that CeO₂ surface oxygen also plays an important role to better the activity of CeO₂-Co₃O₄ catalysts. Among these catalysts, Ce₁Co₁₆ shows the best catalytic activity.

References:

- [1] Thormählen P, Skoglundh M, Fridell E, et al. Low-temperature CO oxidation over platinum and cobalt oxide catalysts [J]. *Journal of Catalysis*, 1999, 188(2): 300.
- [2] Garin F, Simonot L, Maire G. A comparative study of LaCoO₃, Co₃O₄ and LaCoO₃-Co₃O₄. I. Preparation, characterization and catalytic properties for the oxidation of CO [J]. *Applied Catalysis B: Environmental*, 1997, 11(2): 167.
- [3] Lahaye J, Boehm S, Chambrion Ph, et al. Influence of cerium oxide on the formation and oxidation of soot [J]. *Combustion and Flame*, 1996, 104(1-2): 199.
- [4] Liu W, Flytzani Stephanopoulos M. Total oxidation of carbon monoxide and methane over transition metal fluorite oxide composite catalysts: II. catalyst characterization and reaction-kinetics [J]. *Journal of Catalysis*, 1995, 153(2): 317.
- [5] Bernal S, Blanco G, Cauqui M A, et al. Influence of reduction treatment on the structural and redox behaviour of ceria, La/Ce and Y/Ce mixed oxides [J]. *Catalysis Letters*, 1998, 53(1-2): 51.
- [6] Cho B K. Chemical modification of catalyst support for enhancement of transient catalytic activity: nitric oxide reduction by carbon monoxide over rhodium [J]. *Journal of Catalysis*, 1991, 134(1): 74.
- [7] Rossignol S, Madier Y, Duprez D. Preparation of zirconia-ceria materials by soft chemistry [J]. *Catalysis Today*, 1999, 50(2): 261.
- [8] Li M, Liu Z G, Hu Y H, et al. Preparation and char-

- acterization of CeO₂ superfine powder [J]. J. Rare Earths, 2003, 21(6): 654.
- [9] Lamonier C, Ponchel A, D'Huysser A, et al. Studies of the cerium-metal-oxygen-hydrogen system (metal = Cu, Ni) [J]. Catalysis Today, 1999, 50(2): 247.
- [10] Villain S, Cabané J, Knauth P. Solid state electrochemical characterisation of nanostructured silver prepared by cold-rolling and internal oxidation [J]. Scripta Materialia, 1998, 38(6): 1003.
- [11] Jiang Y, Wu Y, Xie B, et al. Moderate temperature synthesis of nanocrystalline Co₃O₄ via gel hydrothermal oxidation [J]. Materials Chemistry and Physics, 2002, 74: 234.
- [12] Jiang X Y, Zhou R X, Yuan J, et al. Catalytic oxidative properties and characterization of CuO/CeO₂ catalysts [J]. J. Rare Earths, 2003, 21(1): 55.
- [13] Bordiga S, Platero E E, Areán C O, et al. Low temperature CO adsorption on Na-ZSM-5 zeolites: An FTIR investigation [J]. Journal of Catalysis, 1992, 137(1): 179.
- [14] Daniells S T, Overweg A R, Makkee M, et al. The mechanism of low-temperature CO oxidation with Au/Fe₂O₃ catalysts: a combined Mössbauer, FT-IR, and TAP reactor study [J]. Journal of Catalysis, 2005, 230(1): 52.
- [15] Haruta M, Tsubota S, Kobayashi T, et al. Low-temperature oxidation of CO over gold supported on TiO₂, α -Fe₂O₃, and Co₃O₄ [J]. Journal of Catalysis, 1993, 144(1): 175.
- [16] Ji L, Lin J, Zeng H C. Metal-support interactions in Co/Al₂O₃ catalysts: A comparative study on reactivity of support [J]. Journal of Physics Chemistry B, 2000, 104(8): 1783.
- [17] Busca G, Lorenzelli V, Escibano V S, et al. FT-113 study of the surface properties of the spinels NiAl₂O₄ and CoAl₂O₄ in relation to those of transitional aluminas [J]. Journal of Catalysis, 1991, 131(1): 167.

* * * * *

Effect of Cycling Loaded Rare Earths on Stripping Process in P507 Extraction System

Wu Sheng^{1,2}, Liao Chunsheng^{1,2}, Jia Jiangtao^{1,2}, Yan Chunhua^{2*} (1. State Key Lab of Rare Earth Materials Chemistry and Applications, Peking University, Beijing 100871, China; 2. Beijing Institute of Founder Rare Earth Science and Technology Co., Ltd., Beijing 100085, China)

Abstract: P507 (HEH[EHP]) is an important extractant for the separation of rare earth and is widely used in industry. Since the complexes of heavy rare earth ions with saponified P507 are so stable that the rare earth ions are difficult to be exchanged and stripped by H⁺ ions. Thus, the cycled extractant loads certain amount of heavy rare earth ion after stripped by acid. This amount of rare earth ions loaded in blank organic phase is named as the "cycling loaded rare earth ions (CLREs)". In the separation process of Tm³⁺, Yb³⁺, and Lu³⁺, the amount of CLREs can be more than 10% of the normal capacity of saponified

organic phase. In fact, CLREs affect the separation efficiency and decrease the purity of the products. Based on the extracting-stripping equilibrium and mass balance, the influence of different process parameters on the amount of CLREs was studied by computer simulation. The results indicate that higher acid consumption and more stripping stages are required to eliminate CLREs. For an industrial practice, however, the acid consumption and the number of stripping stage can be designed by choosing an economic process and controlling CLREs at a reasonable level.

Key words: countercurrent extraction; stripping process; computer simulation; heavy rare earths

(See J. Chin. RE. Soc. (in Chin.), 2006, 24(2): 134 for full text)