

Mesoporous Co–Fe–O nanocatalysts: Preparation, characterization and catalytic carbon monoxide oxidation

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ABSTRACT

A series of mesoporous Co–Fe–O were prepared by the cetyltrimethylammonium bromide (CTAB)-assisted method of nanocrystalline particle assembly, and characterized by X-ray diffraction (XRD), thermogravimetry–differential thermal analysis (TG–DTA), Fourier transform infrared spectroscopy (FT–IR), transmission electron microscopy (TEM) and N₂-sorption analysis techniques. The catalytic properties of the as-prepared samples for CO oxidation were evaluated by using a microreactor–GC system. These mesoporous Co–Fe–O nanocatalysts possesses a wormhole-like mesoporous structure with a narrow pore size distribution and high surface area, exhibiting high catalytic activity for CO oxidation. The catalytic behavior depended on the cobalt species content, the precalcination temperature, the surface area and the particle size of the catalysts. The catalyst of 400 °C-calcined FeCo40 exhibited the highest catalytic activity for CO total oxidation at 140 °C.

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Introduction

Carbon monoxide (CO), which is emitted from the industrial process and the incomplete combustion of hydrocarbon fuels in internal combustion engines of automobiles, is one of the major air pollutants. A little exposure (ppm) of this odorless invisible gas can be lethal. In order to control the toxic emission, catalytic oxidation of CO is an efficient way. The study of the CO oxidation catalysts began with the exploration of a hopcalite-based catalytic converter, a mixture of manganese and copper oxides [1,2]. Recently, more effective noble metal and transition metal, such as Au [3–6], Pt [7–9], Ru [7,10], Pd [11,12], Cu [13–15], and Co [16–19] based catalysts were explored for efficient conversion of CO.

Among the metal oxides, cobalt oxide is the most active for CO oxidation [16–20]. Xie et al. [16] systematically investigated the low temperature oxidation of CO catalyzed by Co₃O₄ nanorods, and the nanorod structure Co₃O₄ exhibit surprisingly high catalytic activity for CO oxidation at temperature as low as –77 °C and remain stable in a moist stream of normal feed gas. Hassan et al. [18] prepared Co₃O₄ nanoparticles by the laser vaporization controlled condensation (LVCC) method, and it gave maximum

conversion of CO to CO₂ at room temperature. Liu et al. [19] prepared a series of Co₃O₄ catalysts by a liquid-precipitation method, and found that the CO conversion of the sample can reach 100% at ambient temperature. Due to the dual functions of iron oxide as a catalyst of carbon monoxide in the presence of oxygen, and in the absence of oxygen, as a direct carbon oxide oxidant by losing the lattice oxygen, iron oxide-based catalysts are attractive candidates amongst the readily available carbon monoxide oxidation catalysts [21–24].

Because of the physical and chemical properties of materials depend not only on the chemical composition but crucially also on their porosity and shape [25], much effort has been focused on tailoring the pore size and external morphology of the materials [26,27]. The mesoporous materials have remarkably large surface areas and narrow pore size distributions so as to give rise to well dispersed and stable metal particles on the surface and as consequence would show an improved catalytic performance. Our recent studies have demonstrated that the high surface area and uniform mesoporosity structure catalysts would give rise to well-dispersed and stable active species nanoparticles on the surface upon calcination and reduction and, as a consequence, would show an improved catalytic performance [14,15,28].

Co–Fe–O nanocomposite and cobalt ferrite nanomaterials were usually used as the magnetic materials [29,30]. However, there is little research focused on using mesoporous Co–Fe–O materials as CO oxidation catalyst. Thus, it is still a challenge to develop

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high-surface-area and mesoporous Co–Fe–O composite materials for the anticipation of enhancing catalytic performance for CO oxidation. In present study, we report a surfactant-assisted method for preparing mesoporous Co–Fe–O nanocatalysts with high surface area. The resulting mesoporous Co–Fe–O materials show high catalytic activity for carbon monoxide oxidation. The influence of cobalt species content and calcination temperature on the catalytic performance of the catalysts is investigated systematically.

Experimental

Catalyst preparation

All chemicals were used as received without further purification. In a typical synthesis procedure of the mesoporous Co–Fe–O nanocatalysts with different Co species content, 6 mmol cetyltrimethylammonium bromide was dissolved into 200 mL distilled water at room temperature, followed by ultrasound irradiation 15 min. Then 10 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and calculated amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added into the above solution under magnetic stirring. After stirring for 0.5 h, 0.2 mol/L sodium hydroxide solution was gradually added until the pH value of the mixed solution was 9. The final suspended solution was aged at 90 °C for 3 h. The precipitate was filtered, washed with hot water, dried in the oven at 100 °C for 12 h, then milled and calcined at different temperatures (200, 300, 400, 500, 600 and 800 °C) for 5 h. The as-prepared catalysts were denoted as FeCo_x ($x = \text{Co}/\text{Co} + \text{Fe}$).

Characterization

X-ray diffraction (XRD) analysis was performed on a Rigaku D/max-2500 diffractometer, with $\text{CuK}\alpha$ radiation at 40 kV and 100 mA in a scanning range of 3–80° (2θ). The diffraction peaks of the crystalline phase were compared with those of standard compounds reported in the JCPDS Date File. Thermogravimetry–differential thermal analysis (TG–DTA) of the sample was conducted on a Rigaku Standard Model thermal analyzer in air atmosphere (flow rate: 90 mL/min; heat rate: 10 °C/min). Fourier transform infrared (FT-IR) spectra were measured on a Bruker VECTOR 22 spectrometer, with the KBr pellet technique, and the ranges of spectrograms were 4000–400 cm^{-1} . Transmission electron microscopy (TEM) analysis was performed on a Philips Tecnai G20 microscope, operating at 200 kV. The samples were dispersed in ethanol and treated with ultrasound for 5 min, and then deposited on a copper grid coated with preformed holey carbon film. N_2 adsorption–desorption isotherms were collected at liquid nitrogen temperature using a Quantachrome NOVA 2000e sorption analyzer. The specific surface areas (S_{BET}) of the samples were calculated following the multi-point BET (Brunauer–Emmett–Teller) procedure. The pore-size distributions were determined from the desorption branch of the isotherms using the BJH (Barett–Joyner–Halenda) method. Before carrying out the measurement, each sample was degassed at 200 °C for more than 6 h. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI 5300 system spectrophotometer with the $\text{MgK}\alpha$ radiation. The operating conditions were kept constantly at 187.5 eV and 250.0 W. In order to subtract the surface charging effect, the C1s peak has been fixed at a binding energy of 284.6 eV.

Catalytic activity test

Catalytic activity tests were performed in a continuous-flow fixed-bed microreactor. A stainless steel tube with an inner diameter of 7 mm was chosen as the reactor tube. About 200 mg catalyst powder was placed into the tube. The reaction gas mixture

consisting of 10 vol% CO balanced with air was passed through the catalyst bed at a total flow rate of 36.6 mL/min. A typical weigh hourly space velocity (WHSV) was 11,000 mL/h/g. After 30 min reaction, the effluent gases were analyzed online by a GC-900A gas chromatograph equipped with a thermal conductivity detector (TCD). The activity was expressed by the conversion of CO.

Results and discussion

Catalyst characterization

Fig. 1 shows the XRD patterns of the surfactant-prepared Co–Fe–O catalysts with different Co species contents after calcination at 400 °C. The XRD patterns of pure Fe_2O_3 and Co_3O_4 samples were also provided for compare purpose. When the Co species content is in the range of 15–30 mol%, the corresponding samples (FeCo_{15} , FeCo_{20} and FeCo_{30}) possess the reflections characteristic of rhombohedral hematite Fe_2O_3 at 33.16°, 40.87° and 49.47° (2θ). With the increase of the Co species content into 40 and 50 mol%, the obtained FeCo_{40} and FeCo_{50} samples show only the reflections characteristic of spinel CoFe_2O_4 phase (JCPDS file 22-1086), without any other impurity phases. FeCo_{40} sample was taken as being representative for the investigation of the thermal stability of the prepared Co–Fe–O catalysts. Fig. 2 shows the XRD patterns of FeCo_{40} catalysts calcined at different temperatures. It is seen that with the increase of the calcination temperature, the spinel CoFe_2O_4 phase with a progressive increase in the relative intensity of the lines indicating an increase of the crystallinity and the growth of particle size by the thermal treatment.

The simultaneous TG–DTA analysis (Fig. 3) of the FeCo_{40} precursor shows a continuous weight loss of 22.9% from 30 to 400 °C. It can be seen from Fig. 3 that the endothermic peak between 30 and 175 °C on DTA, accompanied by a significant weight loss on TG, is attributed to the desorption of water (that may be physical or chemical adsorption on the interparticle surface of the sample or reside the mesopores). The main weight loss between 175 and 400 °C on the TG curve, accompanied with a strong exothermic peak at 219 °C and a shoulder around 255 °C, can be attributed to the decomposition of the surfactant and the combustion of carbon species. No crystalline phase transformation is observed. After 400 °C, the weight of the precursor no longer changes, which indicates that the carbon species (surfactant molecules) in the samples could be completely removed after calcination at 400 °C in air. Since calcination at high temperature

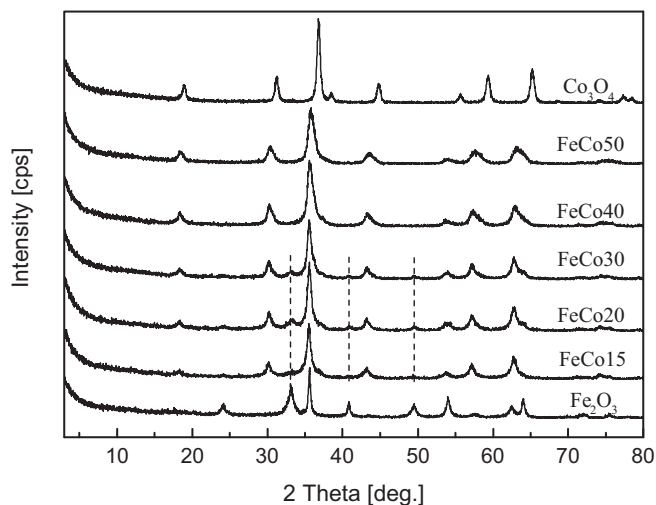


Fig. 1. XRD patterns of FeCo_x catalysts with different Co species contents calcined at 400 °C.

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