Synthesis and characterization of mesoporous Fe–Co mixed oxide nanocatalysts for low temperature CO oxidation

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ABSTRACT

The catalytic oxidation of CO into CO_2 on mesoporous Fe–Co mixed oxide nanocatalysts at low temperature was carried out. The catalysts with different ratios of Co_3O_4 (1–30 wt.%) were prepared by a simple co-precipitation method. The original and calcined catalysts were characterized by TG, DTA, XRD, TEM, VSM, N_2 sorption analysis, surface chemisorbed oxygen and dc electrical conductivity measurements. The results revealed that the addition of Co_3O_4 to Fe_2O_3 monotonically increases the amount of surface chemisorbed oxygen, electrical conductivity and catalytic activity of the nanocatalysts. The role of the active redox sites established in these nanocatalysts such as, Co^{3+}/Co^{2+}, Fe^{3+}/Fe^{2+} and Co^{3+}/Fe^{2+} which are responsible for such modification was discussed. The magnetic studies indicated that the Fe–Co mixed oxide nanocatalysts exhibited ferromagnetic nature and the catalyst containing 30 wt.% Co_3O_4 calcined at 600 °C possessed the highest saturation magnetization ($M_s = 51.5$ emu g^{-1}). In addition the kinetic data illustrated that, the activation energy values of CO oxidation gradually decreased with increasing of Co_3O_4 content. Moreover, the catalytic behavior under different atmospheres during calcination was also studied.

1. Introduction

Carbon monoxide (CO) is a strongly toxic gas and it is one of the major air pollutants. It is emitted from the industrial processes, the incomplete combustion of hydrocarbon fuel in internal combustion engines of automobiles, volcanic activity and bushfires. A little exposure (ppm) of this invisible, odorless gas can be lethal. Thus, in particular, the oxidation of CO into CO_2 has attracted the most attention due to its relevance in many industrial applications.

Both platinum group metals and transition metal oxides have been found to catalyze the CO oxidation. In spite of the high conversion values, the high cost, their sensitivity to sulfur poisoning as well as the limited availability of noble metals limit their extensive application. Thus the development of active and stable catalysts without noble metals for low temperature CO oxidation under an ambient atmosphere remains a significant challenge. Nanocomposites of transition metal oxides characterized by their small particle size, high surface area, and perhaps more importantly, more densely populated surface coordination unsaturated sites and less costly alternatives, could potentially provide improved catalytic performance (Biabani-Ravandi et al., 2013a,b; Cao et al., 2014; Biabani-Ravandi and Rezaei, 2012; Cheng et al., 2007). Among the transition metal oxide catalysts, iron oxides are one of the cheapest materials for oxidation of CO, but pure iron oxides have a relatively low activity at low temperatures (below 200 °C). Due to the dual function of iron oxide as a catalyst of CO in the presence and absence of oxygen, iron oxide-based catalysts are attractive candidates amongst the readily

available CO oxidation catalysts (Li et al., 2003, 2011; Cao et al., 2011; Weiliang et al., 2013; Abdel Halim et al., 2007; Kwon et al., 2007).

On the other hand it was reported that, the catalytic oxidation of CO over cobalt oxide catalyst has also been one of the hottest spots in the field of heterogeneous catalysis and nanocatalysis. Co_3O_4 showed the highest catalytic activity for the combustion of CO and of organic compounds and it may be included in the formulations of catalyst for treatment of waste gases (Lou et al., 2014; Royer and Duprez, 2011; Lv et al., 2013; Hu et al., 2010; Yu et al., 2009; Xie et al., 2009; Umegaki et al., 2016; Wang et al., 2007).

However, a great deal of fundamental research focused on mixed oxide catalysts in the field of heterogeneous catalysis. These mixed systems may be more active than their separate components (Biabani-Ravandi et al., 2013a,c; Salker and Niak, 2009). Accordingly, it was reported that mixing of Co_3O_4 with iron oxide enhanced the catalytic activity of iron oxide even more than pure Co_3O_4 (Cao et al., 2014; Biabani-Ravandi and Rezaei, 2012; Biabani-Ravandi et al., 2013b; Qwobe et al., 2015; Biabani et al., 2012). Cao et al. (2014) have prepared and characterized Co–Fe–O mesoporous nanocatalysts. They concluded that, the catalytic behavior depended mainly on the content of Co species and the precalcination temperature. In addition, the catalysts containing 40 wt.% Co_3O_4 calcined at 400 °C exhibited the highest catalytic oxidation of CO. Biabani-Ravandi et al. (2013c), have prepared Fe–Co–O nanocatalysts and reported that cobalt oxide mixed with iron oxide (1/5 molar ratio) completely oxidized CO into CO_2 at 200 °C. Moreover, The same working group (Biabani-Ravandi et al., 2013b) has reported that, the addition of Co_3O_4 to Fe_2O_3, with a molar ratio of 1:1 greatly enhances both the structural and catalytic properties and total CO oxidation was achieved at 180–200 °C. Furthermore, the catalytic oxidation of CO over iron-cobalt nanocatalysts was investigated by Biabani-Ravandi and Rezaei (2012). They attributed the high catalytic activity of the mixed oxides than the pure oxides to the synergistic effect between the two oxides and the temperature at which 100% CO oxidation was ≥200 °C. Moreover, optimization of preparation conditions of Fe–Co mixed oxide nanoparticles was investigated by Biabani et al. (2012). Under the optimized condition, the complete oxidation of CO was achieved at 225 °C.

Therefore, the challenge of this study was devoted to develop a high surface area and mesoporous Fe–Co mixed oxide nanocatalysts with high catalytic performance for CO oxidation at lower temperatures than that previously reported.

2. Experimental

2.1. Catalysts preparation

Pure Fe_2O_3, pure Co_3O_4 and Fe_2O_3 mixed with different wt.% of Co_3O_4 (1–30 wt.%) were prepared by co-precipitation method (Biabani-Ravandi and Rezaei, 2012; Biabani-Ravandi et al., 2013b). In a typical preparation, calculated amounts of $Fe(NO_3)_3 \cdot 9H_2O$ (Merck, 98%) and $Co(NO_3)_2 \cdot 6H_2O$ (WinLab, 99%) were dissolved in bidistilled water and the resulting solutions were heated to 70 °C. Then an aqueous solution of potassium carbonate (0.2 M) was added to the mixed nitrate solutions, under continuous stirring, at a rate of 2–3 ml min^{-1} at 70 °C until pH 8.2 ± 0.1 was achieved. The resulting precipitates were aged at this pH for 2 h and then filtered and washed with warm bidistilled water several times to remove excess ions.

The precipitates were dried at 110 °C overnight before calcined at 300–600 °C in air atmosphere for 3 h.

2.2. Catalyst characterization

2.2.1. Thermal analysis
Thermogravimetery (TG) and differential thermal analysis (DTA) were carried out using a Shimadzu Thermal Analyzer (TA 60H, Japan) apparatus. The samples were analyzed under air atmosphere with a flowing rate of 30 ml min^{-1} and a heating rate of 10 °C/min. α-Al_2O_3 was used as a reference material in this technique.

2.2.2. X-ray diffraction (XRD)
An X-ray investigation of the individual and mixed nanocatalysts precalcined at 300–600 °C was conducted using a Philips diffractometer (Model PW 2103, $\lambda = 1.5418$ Å, 35 KV and 20 mA) with a source of CuKα_1 radiation (Ni Filtered). Crystallite size can be estimated from the full width at half maximum (FWHM) of the X-ray diffraction line. The broadening of the FWHM is inversely proportional to the average crystallite size (D) as predicted by the well-known Scherer's formula (Cullity, 1967). The grain size D is calculated from the following relation:

$$D_{XRD} = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where β is the observed angular width at half maximum intensity of the peak, K is a dimensionless number, which is equal to 0.89, λ is the X-ray wavelength (1.5418 Å for Cu Kα) and θ is the diffraction angle.

2.2.3. Nitrogen sorption
Nitrogen adsorption–desorption isotherms were measured at −196 °C by the Quantachrom Instrument Corporation, USA (Model Nova 3200). Test samples were thoroughly out gassed for 2 h at 250 °C to a residual pressure of 10^{-5} Torr. The porosity of the catalysts was determined from the desorption curve using Nova enhanced data reduction software (Version 2.13).

2.2.4. Surface chemisorbed oxygen measurement
The surface chemisorbed oxygen was measured by the previously described method (Said et al., 1983, 2014). This method consists in reducing the surface chemisorbed oxygen on the catalyst surface with hydrazine and measuring the amount of nitrogen gas evolved with the aid of gasometric technique.

2.2.5. Transmission electron microscope (TEM)
A TEM specimen was prepared by mixing the sample powder in ethanol then sonicated for about 10 min then placing a drop onto a formvar-backed carbon coated copper grids. The TEM pictures were taken by a TECNAI G^2 spirit TWIN at 120 kV accelerating voltage and conducted by VELETA camera.

2.2.6. Electrical conductivity
The electrical conductivity measurements were carried out as the method described by Said et al. (1983).

2.2.7. Magnetization measurements
Magnetization measurements were carried out at room temperature (27 °C) using a vibrating sample magnetometer (VSM, Lakeshore 7410) under an applied magnetic field of 20 kOe.