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Article

Low temperature CO oxidation over mesoporous CuFe_2O_4 nanopowders synthesized by a novel sol-gel method

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ABSTRACT

Mesoporous CuFe_2O_4 solid solution nanopowders with high specific surface areas were synthesized by a novel, very simple and inexpensive sol-gel route using propylene oxide as gelation agent, and used as the catalyst in low temperature CO oxidation. The samples were characterized by X-ray diffraction, N_2 adsorption-desorption, thermogravimetric/differential thermal analysis, Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, and temperature-programmed reduction. The results revealed that the samples have a nanocrystalline structure with crystals in the range of 10 to 25 nm, and that all the catalysts have mesoporous pores. The addition of Cu into iron oxide affected its structural and catalytic properties. The sample containing 15 mol% Cu showed the highest specific surface area and catalytic activity, and showed high catalytic stability in low temperature CO oxidation.

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1. Introduction

CO is an air pollutant that is extremely dangerous for human life and environment, and it has affinity for combining with hemoglobin to prevent the transport of oxygen to cells, which causes death. CO is produced in industrial processes and hydrocarbon fuel combustion. One of the best ways to control its environmental pollution and harm is by its conversion to CO_2 , which is much less hazardous than CO. Noble metal catalysts such as Au, Pt, and Pd are the best candidates for CO oxidation, and are able to remove it at ambient temperatures [1–3]. However, these metals are rare, very expensive, and very sensitive to sulfur poisons [4]. Hence, in the last decade, much attention has been given to replacing them with transition metal oxides, particularly CuO, Co_3O_4 , MnO_2 , and Fe_2O_3 [4–9]. Transition metal oxides supported on Fe_2O_3 such as $\text{CuO-Fe}_2\text{O}_3$ and

$\text{Co}_3\text{O}_4\text{-Fe}_2\text{O}_3$ are highly active for CO oxidation at low temperature through a synergistic effect, and can be suitable alternatives for noble metal catalysts [8,9]. Therefore, many studies have focused on supported transition metal-based catalysts, specially supported Cu on Fe_2O_3 . However, it is known that pure Fe_2O_3 has poor catalytic activity for CO oxidation at low temperature. The structure modification of the Fe_2O_3 lattice by doping with copper oxide improved the catalytic activity of Fe_2O_3 at low temperature [9,10].

In this paper, we report the preparation of nanostructured mesoporous CuFe_2O_4 solid solution powders with high specific surface areas and different Cu/Fe molar ratios by a novel, very simple and inexpensive sol-gel route using propylene oxide as gelation agent. Low temperature CO oxidation over CuFe_2O_4 was investigated in detail.

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2. Experimental

2.1. Catalyst preparation

Mesoporous CuFe_2O_4 solid solutions with a high specific surface area and different Cu/Fe molar ratios were synthesized by a novel and simple sol-gel route using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as Fe and Cu precursors, respectively, and propylene oxide as gelation agent. In a typical synthesis, 10 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with a calculated amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved in the appropriate amount of distilled water at room temperature. After stirring for 15 min, an amount of propylene oxide (propylene oxide/(Fe+Cu) molar ratio = 11) was added to the solution. The gel was formed within 5 min. The resulting gel was aged at room temperature for 1 h and then dried in air at 80 °C for 48 h, and finally calcined at 300 °C with a ramp rate of 3 °C/min for 5 h in an air atmosphere. The nominal contents of CuO were 5, 10, 15, 25, 30, and 40 mol%, and the corresponding catalysts were denoted as FeCu5, FeCu10, FeCu15, FeCu25, FeCu30, and FeCu40, respectively.

2.2. Catalytic characterization

X-ray diffraction (XRD) analysis was performed on a PANalytical X'Pert-Pro X-ray diffractometer with a $\text{Cu-K}\alpha$ monochromatized radiation source and a Ni filter in a scanning range $2\theta = 20^\circ$ – 80° . Temperature programmed reduction (H_2 -TPR) was performed in an automatic apparatus (Micromeritics, Chemisorb 2750) equipped with a thermal conductivity detector (TCD). In the TPR measurement, 100 mg catalyst was subjected to a heat treatment (10 °C/min) in a gas flow (30 ml/min) containing a mixture of 10% H_2 -90% Ar. Prior to the TPR experiment, the sample was thermo-treated under an inert atmosphere (Ar) at 200 °C for 1 h. The H_2 consumption amount during the reduction was measured using a TCD. Infrared (FT-IR) spectra were recorded on a NEXus Fourier transform infrared (FTIR) spectrophotometer using KBr pellets containing 1 wt% sample in KBr. Thermogravimetric (TG) and differential thermal analysis (DTA) of the catalysts were carried out on a Netzsch STA 409 model system at a heating rate of 10 °C/min in a static air atmosphere. N_2 adsorption-desorption analysis was carried out at -196°C using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). The morphology of the samples was characterized by scanning electron microscopy (SEM, VEGA@TESCAN). The transmission electron microscope (TEM) images were obtained on a JEM-2100UHR instrument.

2.3. Catalytic activity test

The catalytic activity tests for CO oxidation reaction were carried out on a continuous flow fixed bed quartz reactor at ambient pressure. The reactor was charged with 100 mg of the catalyst sieved to 35–70 mesh. The reaction gases consisted of 20 vol% O_2 and 2 vol% CO balanced with 78 vol% inert gas. The catalysts were pretreated in 20 vol% O_2 balanced with He at 300 °C for 2 h prior to exposure to the reaction gas. The ac-

tivity tests were performed at different temperatures with steps of 25 °C that were kept for 15 min at each temperature. The gas composition of reactants and products were analyzed online using a gas chromatograph (Varian 3400) equipped with a TCD and a molecular sieve 5A column.

3. Results and discussion

3.1. Catalyst characterization

Figure 1 shows the XRD diffraction patterns of the Fe-Cu mixed oxide nanocatalysts with different Cu/Fe molar ratios after calcination at 300 °C. The diffraction pattern of pure Fe_2O_3 indicated the presence of hematite iron oxide (α - Fe_2O_3) and maghemite iron oxide (γ - Fe_2O_3) with the rhombohedral and cubic crystalline system, respectively. The reflections at 24.25° , 33.37° , 35.77° , 40.99° , 49.75° , 54.25° , 57.85° , 62.59° , 64.21° , 72.13° , and 75.67° showed the main reflections of α - Fe_2O_3 , which are due to the (012), (104), (110), (113), (024), (116), (018), (214), (300), (1010), and (220) planes in the rhombohedral crystalline system, respectively. The reflections at 30.67° , 35.77° (with interference with the reflection of α - Fe_2O_3 (110) planes and their intensities increased), 43.75° , 57.49° , and 63.01° were due to the reflections of the (220), (311), (400), (511), and (440) γ - Fe_2O_3 planes of the cubic crystalline system. As compared with the peaks of pure Fe_2O_3 , adding 5 mol% Cu caused the peaks due to α - Fe_2O_3 in the FeCu5 sample to be shifted from 33.37° , 54.25° , and 62.59° to 33.13° , 54.13° , and 62.95° , respectively, and the peaks due to γ - Fe_2O_3 to be shifted from 30.67° , 43.75° , 57.49° , and 63.01° to 30.61° , 43.63° , 57.61° , and 63.13° , respectively.

These shifts in peak positions indicated a change of the lattice parameters and the incorporation of Cu atoms into the lattice of Fe_2O_3 to form the CuFe_2O_4 spinel solid solution with the cubic crystalline system. When the Cu was added in the range of 5 to 25 mol%, the results were similar to FeCu5 sample. With the addition of higher amounts of Cu up to 30 mol%, excess Cu was crystallized separately and CuO characteristic peaks appeared. With increasing Cu content up to 40 mol%, the

Fig. 1. XRD patterns of the CuFe_2O_4 catalysts with different CuO contents calcined at 300 °C.

Table 1Structural properties and catalytic activities of the CuFe_2O_4 catalysts.

Sample	Average crystalline size (nm)	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)	T_{100} ($^{\circ}\text{C}$)
Fe_2O_3	24	48.39	0.12	10.15	490
FeCu5	19	88.43	0.2	9.35	285
FeCu10	12	112.34	0.21	7.48	280
FeCu15	10	116.90	0.21	7.06	190
FeCu25	11	106.87	0.22	8.25	210
FeCu30	12	99.35	0.16	6.68	235
FeCu40	16	49.91	0.1	8.51	260

peak intensity of CuO was increased. The average particle sizes were also calculated from the half-width of the main diffraction peaks using the Scherrer formula. The results are presented in Table 1.

In order to study the redox behavior and CuO- Fe_2O_3 interactions of the catalysts, H_2 -TPR analysis was carried out. Figure 2 shows H_2 -TPR profiles of catalysts with different CuO contents. The reduction profile of pure Fe_2O_3 exhibited two major reduction peaks. The first peak at 350–450 $^{\circ}\text{C}$ is from the reduction of Fe_2O_3 to Fe_3O_4 , and the broad peak at above 600 $^{\circ}\text{C}$ was attributed to the reduction of Fe_3O_4 to Fe^0 [11]. After adding 5 mol% Cu in the FeCu5 sample, a sharp peak at 200 $^{\circ}\text{C}$ appeared. This peak can be ascribed to the reduction of CuFe_2O_4 to Cu 0 and Fe_2O_3 [12]. Fe_2O_3 was reduced to Fe_3O_4 in another step, and finally Fe_3O_4 was reduced to metallic iron at higher temperatures. In comparison with pure Fe_2O_3 , the peaks related to the reduction of Fe_2O_3 to Fe^0 in the FeCu5 sample were shifted to a lower temperature. This observation was explained by a synergistic effect between CuO and Fe_2O_3 , in which CuO promoted the reduction of Fe_2O_3 at a lower temperature. When Cu content was in the range of 5 to 15 mol%, the results were similar to the FeCu5 sample. However, with the addition of higher amounts of Cu, the intensity of the peak due to the reduction of CuO, which is present in CuFe_2O_4 , increased. With increasing Cu content up to 25 mol%, another peak below 200 $^{\circ}\text{C}$ appeared in the FeCu25 sample. In the FeCu25 sample, excess Cu is crystallized separately and CuO characteristic peaks appeared. The two step reduction peaks indicated the existence of two CuO species. The first peak below 200 $^{\circ}\text{C}$ is due to the reduction of CuO because of the higher reducibility of CuO compared with

CuO present in the structure of the CuFe_2O_4 solid solution. This is consistent with the XRD result. For the FeCu30 and FeCu40 samples, the results were similar to the FeCu25 sample. In addition, with increasing Cu content, the intensity of peak due to the reduction of the CuO species increased.

Figure 3 shows the FT-IR spectra of the as-prepared and calcined FeCu15 samples. A broad peak on the as-prepared sample was seen at 3410.43 cm^{-1} , which is due to the stretching vibration of the hydroxyl groups of alcohol (note: in the gelation process, it is probable that first propylene oxide is protonated; then this intermediate structure undergoes irreversible ring opening reaction by nucleophilic attack by Cl^- and finally 1-chloro-2-propanol is produced) and adsorbed water. The weak band on the calcined sample is due to adsorbed water. Similarly, the peak at 1625.79 cm^{-1} was attributed to adsorbed water, which decreased after calcination. The peak at 1080.77 cm^{-1} was assigned to the stretching vibration of C–O, and it disappeared after calcination. In the as-prepared sample, two peaks in the region of ~ 2925.61 cm^{-1} were due to the stretching vibrations of CH_3 and CH_2 groups in propylene oxide and 1-chloro-2-propanol, which were not seen after calcination. Similarly, the peak at 1382.16 cm^{-1} is related to the bending vibration of CH_3 , which was also removed after calcination. Two peaks in the region of 400 to 600 cm^{-1} were attributed to the metal-oxygen bonding vibration at octahedral and tetragonal holes in the spinel structure, which were sharpened after calcination at 300 $^{\circ}\text{C}$.

Figure 4 shows the TG-DTG and DTA curves of the as-prepared FeCu15 sample. The TG curve showed weight losses (approximately 10%) in several steps in the region of

Fig. 2. H_2 -TPR profiles of the CuFe_2O_4 catalysts. **Fig. 3.** FT-IR spectra of the as-prepared (1) and calcined (2) FeCu15 catalyst.

Fig. 4. TG-DTG (a) and DTA (b) curves of the as-prepared FeCu15 catalyst.

~50 to 165 °C, corresponding to a broad endothermic peak centered at 130 °C in the DTA curve. This endothermic peak is due to the evaporation of adsorbed water on the surface and water trapped in the pores. With increasing temperature, a rapid weight loss of 21% in the region of ~165 to 270 °C was found, which was attributed to propylene oxide (and related compounds derived from it during the sol-gel process) combustion. Furthermore, the TG curve displayed a weight loss (14%) in the region of ~270 to 360 °C, corresponding to the crystallization of metal hydroxide into metal oxide and the removal of residual hydroxide groups. The weight loss from 360 to 430 °C was ascribed to the decomposition of nitrates derived from copper precursors. There was an endothermic peak at 620 °C in the DTA curve, while correspondingly there was no obvious weight loss in the TG curve in this region. This was attributed to the phase transformation from γ -Fe₂O₃ to α -Fe₂O₃.

The specific surface area analysis demonstrated that the addition of Cu to Fe₂O₃ increased the surface area of all the samples. In fact, the addition of Cu to Fe₂O₃ can control and promote the structure of pure Fe₂O₃ and induced an increase in the surface area of the samples. As can be seen in Table 1, the specific surface areas of all samples were higher than that of pure Fe₂O₃. Furthermore, with increasing Cu content up to 15 mol%, the specific surface area of the samples increased. However, with a larger Cu loading, excess CuO coated some of the active sites and these have a negative effect on the specific surface area and catalytic activity.

Figure 5 shows the N₂ adsorption isotherms and pore size distributions of the catalysts. According to the IUPAC classification, the N₂ isotherm is a type IV isotherm with a large type H3 hysteresis loop. This type of hysteresis is usually found with solids consisting of aggregates or agglomerates of particles forming slit shaped pores (plates or edged particles like cubes), and with a non-uniform size and/or shape. The pore size dis-

Fig. 5. N₂ adsorption isotherms (a) and pore size distributions (b) of the CuFe₂O₄ catalysts with different CuO contents.

tributions of the samples were obtained by the BJH method. All the catalysts have mesoporous pores. Pure Fe₂O₃ displayed a wide pore size distribution. The addition of Cu to Fe₂O₃ promoted the structure and resulted in smaller pores and a narrower pore size distribution.

With increasing CuO content to 15 mol%, the specific surface area of samples increased from 48.39 to 116.90 m²/g, accompanied by a decrease of pore size and increase of pore volume (Table 1). With more increase in CuO content from 15 to 40 mol%, the specific surface area of samples decreased to 49.91 m²/g, accompanied by an increase of the particle and pore size and decrease of the pore volume. Figure 6 shows the

Fig. 6. SEM image of the FeCu15 catalyst.

Fig. 7. TEM images of the FeCu15 catalyst with different magnifications.

SEM image of the FeCu15 sample. It is seen that the particles are in the nanometer scale.

TEM images of the FeCu15 sample with different magnifications are shown in Fig. 7. It clearly demonstrated that a crystal structure with spherical shape was formed. Also, the sample showed a nanocrystalline structure with crystal sizes in the range of 10 to 25 nm.

3.2. Catalytic activity

Figure 8 shows the catalytic activity for low temperature CO oxidation as a function of reaction temperature over the CuFe_2O_4 catalysts. Their catalytic activity increased with reaction temperature. The temperatures for the complete conversion of CO (T_{100}) are presented in Table 1.

As can be seen in Fig. 8, the activities of all the catalysts

Fig. 8. Catalytic activity for low temperature CO oxidation over CuFe_2O_4 catalyst. GHSV = $60000 \text{ ml g}^{-1} \text{ h}^{-1}$.

Fig. 9. Effect of GHSV on the catalytic activity of the FeCu15 catalyst.

were much higher than that of pure Fe_2O_3 . Pure Fe_2O_3 showed a low catalytic activity in low temperature CO oxidation. In general, the addition of CuO to Fe_2O_3 can control and promote the structure to form a CuFe_2O_4 solid solution with high specific surface area, which leads to enhanced catalytic activity through a synergistic effect. In addition, increasing the Cu content up to 15 mol% increased the CO conversion. The catalyst with 15 mol% Cu showed the highest specific surface area and activity in low temperature CO oxidation with CO total conversion at 190°C . The results showed that with further increase in CuO content, the catalytic activity decreased because excess CuO covered some active centers and also caused an increase in particle size and decrease in specific surface area.

In order to investigate the influence of residence time on the catalytic activity, the CO oxidation reaction was preformed over the FeCu15 catalyst with different gas hourly space velocities (GHSV). The results are shown in Fig. 9. With an increase in GHSV from $60000 \text{ ml g}^{-1} \text{ h}^{-1}$ to $75000 \text{ ml g}^{-1} \text{ h}^{-1}$, the catalytic activity decreased due to the decrease in residence time.

In order to investigate the stability and influence of reaction time on the catalytic activity of the FeCu15 catalyst, CO oxidation reaction was carried out as a function of reaction time at 180°C . The result is shown in Fig. 10. The catalyst has very good stability during the reaction time of 50 h without any decrease in CO conversion. The high catalytic stability of this catalyst was probably due to the spinel structure of CuFe_2O_4 . This

Fig. 10. Long term stability of the FeCu15 catalyst in low temperature CO oxidation. Reaction conditions: GHSV = $60000 \text{ ml g}^{-1} \text{ h}^{-1}$, $T = 180^\circ\text{C}$.

Graphical Abstract

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Low temperature CO oxidation over mesoporous CuFe_2O_4 nanopowders synthesized by a novel sol-gel methodEhsan Amini, Mehran Rezaei*, Mohammad Sadeghinia
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CuFe_2O_4 solid solution nanoparticles were synthesized by a very simple and cheap method. The nanoparticles exhibited good catalytic activity and stability during low temperature CO oxidation.

result indicated that CuFe_2O_4 is a very stable catalyst for low temperature CO oxidation.

4. Conclusions

Mesoporous CuFe_2O_4 solid solution nanopowders with high specific surface areas were prepared by a novel, very simple and inexpensive sol-gel route using propylene oxide as gelation agent. The powders showed the presence of mesopores and they have a nanocrystalline structure with crystal sizes in the range 10 to 25 nm. Pure Fe_2O_3 has a low catalytic activity in low temperature CO oxidation. The addition of CuO into Fe_2O_3 promoted the structure and formed a CuFe_2O_4 solid solution powder with a high specific surface area, which led to enhanced catalytic activity through a synergistic effect. The catalyst with 15 mol% Cu, which has the highest surface area, has the highest activity with CO total conversion at 190 °C. This catalyst showed good catalytic stability with no decrease in low temperature CO oxidation activity.

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