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CuO catalysts supported on activated red mud for efficient catalytic carbon monoxide oxidation

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HIGHLIGHTS

- Red mud was activated and employed as the support for efficient CuO catalyst system.
- High activity was obtained for CO oxidation on the resultant CuO/activated red mud catalysts.
- The catalyst calcined at 200 °C with 20% CuO loading amount possessed the highest catalytic activity.
- The CuO content and precalcination temperatures had significant impacts on the catalytic properties.

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ABSTRACT

Red mud was activated by digestion in hydrochloric acid and re-precipitation with ammonia, and the activated red mud (ARM) was used as the support for preparation of CuO/ARM catalysts by a simple deposition–precipitation method. The prepared catalysts possessed well-structured porosity and high surface area, as characterized by X-ray diffraction, Fourier transform infrared spectroscopy, H_2-temperature-programmed reduction, X-ray photoelectron spectroscopy, and nitrogen sorption techniques. High activity was observed for CO oxidation on the resultant CuO/ARM catalysts, and the CuO content and precalcination temperature had significant impacts on the catalytic properties. The catalyst calcined at 200 °C with 20% CuO loading amount demonstrated the highest catalytic activity, suggesting the CuO/ARM as a promising catalyst in the CO oxidation reaction, on the sake of the utilization of waste solids with much low cost of ARM.

1. Introduction

As a common component of automotive exhaust and industrial waste gas, carbon monoxide (CO) is largely harmful to human health and environment, and the catalytic oxidation of CO is considered to be one of the most efficient routes for controlling the CO emission [1,2]. Over the last several decades, many kinds of noble metals (Pt, Au, Pd, etc.) exhibit superior catalytic activity for CO oxidation [3–8]. However, the high cost, low availability, and poor stability at elevated temperature seriously impede their wide application. Recently, CuO-based catalysts have been demonstrated to be the very promising alternatives to substitute for the noble metal catalysts, due to their low cost, high activity, and good stability [9–12]. And many kinds of supports, such as ceria, alumina, titania, mesoporous silica and so on, have been widely used for preparation of supported CuO catalysts [13–15]. And the nature of these supports can significantly affect their catalytic performance, as well as the reaction mechanism. Schubert et al. [16] clarified the influence of the support materials (SiO_2, Al_2O_3, MgO, Fe_2O_3, TiO_2, NiO_x, CoO_x) on the activity of CO oxidation and divided them into “inert” and “active” support materials. Fu et al. [17] also demonstrated that the interface-confined coordinatively unsaturated ferrous sites together with the metal supports were active for oxygen molecule activation, thus creating highly reactive oxygen atoms, which was highly efficient for catalytic CO oxidation. To date, many supports have been demonstrated to be beneficial for CO oxidation, but the exploitation of new catalyst support with much low cost and rich porous structure is still a challenge.

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Red mud (RM) is a large scale waste product from alumina production, which is a hazardous material with high alkalinity [18]. While, RM contains a relatively large amount of aluminum and iron, which can be used as a potential alternative catalyst for various catalytic reactions [19,20]. Before using it, activation procedures are usually used to increase its surface area, as well as minimize the effect of its composition. Up to now, the activated red mud (ARM) has been utilized for many different kinds of catalytic reactions, for example, hydrogenation [21], hydrodechlorination [22], catalytic combustion [23] and hydrogen production [24,25]. Recently, Sushil et al. [26] observed that the hydroxylated phases and the high surface area of the acid-digested red mud catalysts were beneficial to the enhancement of catalytic activity for CO oxidation. Indeed, Cao et al. [27] investigated the removal of CO on mesoporous CuO–Fe_2O_3 composite catalysts with high activity and thermal stability. Qiao et al. [28] prepared ferric hydroxide supported CuO catalysts for preferential oxidation of CO in the presence of H_2, and the CuO/$Fe(OH)_x$ catalyst exhibited superior catalytic performance. RM contains a large amount of iron, which can be used as a promising catalyst carrier for CuO in catalytic oxidation of CO. Very recently, Cao et al. [29] prepared CuO/modified red mud by an impregnation method, however, this catalyst exhibited relatively low catalytic activity. So, it is urgent to exploit a more efficient CuO-red mud catalyst system by a simple method.

In this work, the as-received RM was activated through a modified Pratt and Christoverson method [30], and employed as support of CuO catalysts for CO oxidation. The catalytic performances of the CuO/ARM catalysts with different loading amount were tested, and the effects of the precalcination temperature of the catalysts were investigated. The resultant catalysts with much low cost exhibit high activity in the oxidation of CO, suggesting a practical potential in the fields of the environmental catalyst system.

2. Experimental section

2.1. Catalysts preparation

RM was supplied by Henan Zhongmei Aluminum Co. (China). Its main constituents are Al_2O_3 (23.25%), SiO_2 (16.94%), CaO (16.94%), Fe_2O_3 (15.05%), TiO_2 (4.27%), Na_2O (3.72%), MgO (1.93%) and K_2O (1.82%). Commercial CuO, HCl and NH_4OH were purchased from Tianjin Guangfu Fine Chemical Research Institute.

For RM activation, 20 g of RM was added into 100 ml of distilled water, followed by adding 100 ml of 6 M HCl solution. The mixture was digested at 90 °C for 2 h. Then, ammonium hydroxide was added dropwise into the mixture until the solution pH around 8. The precipitate was filtered, washed with distilled water for several times, and dried at 120 °C overnight in air, which was denoted as ARM.

The CuO/ARM catalysts were prepared by a simple deposition–precipitation (DP) method. In a typical preparation process, 1 g of ARM was firstly added into 50 ml distilled water under stirring for 15 min, followed by the addition of the calculated amount of $Cu(NO_3)_2{\cdot}3H_2O$. After further stirring for 30 min, 0.5 M Na_2CO_3 solution was gradually added to adjust the pH around 9. Then, the mixture was stirred for another 1 h, sonicated for 30 min, washed with excessive water until pH ≈ 7. The resulting samples were dried at 120 °C overnight, and subsequently calcined at 200 °C for 2 h. The corresponding catalysts were denoted as CuO/ARM-*x*%, where *x* represents the content of CuO (1–30 wt%). Furthermore, in order to investigate the effect of the precalcination temperature, CuO/ARM-20% was calcined at different temperature (300, 400 and 500 °C) for 2 h.

2.2. Characterization

Powder X-ray diffraction (XRD) analysis was measured on a Bruker D8 Focus diffractometer, with Cu K_α radiation (λ = 0.15418 nm), operating at 40 kV and 40 mA with a step size of 12° min^{-1}.

Nitrogen sorption experiments at 77 K were performed on a Quantachrome Autosorb-1MP sorption analyzer. Prior to the measurements, the samples were degassed at 200 °C overnight. The surface area (S_{BET}) was estimated according to the Brunauer–Emmett–Teller (BET) method from the adsorption branch in the relative pressure of P/P_0 = 0.05–0.3, the total pore volume (V_{total}) was obtained from the volume adsorbed at a relative pressure (P/P_0) of 0.99, and the pore size distribution curves were calculated by the non-local density functional theory (NLDFT).

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a FEI Tecnai G2 F20 at 200 kV. The elemental mapping images of the sample were measured by an Oxford INCA energy dispersive spectroscopy (EDS). The Fourier transform infrared (FT-IR) spectroscopy was carried out using a Bruker Tensor 27 spectrometer with 128 scans at a 4 cm^{-1} resolution, and the ranges of spectrograms were 4000–400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) experiment was performed using a Kratos Axis Ultra DLD (delay line detector) spectrometer equipped with an Al-$K\alpha$ X-ray source (1486.6 eV), and survey spectra were recorded with a pass energy of 160 eV, and high resolution spectra with a pass energy of 40 eV.

The thermogravimetry (TG) analysis was performed on a TA SDT Q600 instrument. All the samples were heated with a rate of 10 °C min^{-1} from ambient temperature to 800 °C using α-Al_2O_3 as the reference. Raman spectra were measured by Raman microscope (DXR, Thermo Fischer Scientific) with excitation at 532 nm from an argon-ion laser. The hydrogen temperature-programmed reduction (H_2-TPR) measurements were performed in a quartz U-tube by using a QuantachromeChemBET 3000 analyzer. Before the tests, 50 mg of sample was pretreated in helium gas (20 mL min^{-1}) at 200 °C for 2 h. Then, the sample was reduced under 10% H_2/Ar flowing (20 mL min^{-1}) at 10 °C min^{-1} from room temperature to 1000 °C. The hydrogen consumption amount was detected by a thermal conductivity detector (TCD). For comparison, 14.8 mg of commercial CuO powders were taken for H_2-TPR measurement.

2.3. Catalytic tests

The catalytic performances of CuO/ARM catalysts in CO oxidation reaction were performed in a tubular flow fixed-bed reactor (inner diameter, 6 mm) at atmospheric pressure. 0.2 g catalyst power was placed in the flat-temperature zone of the tubular reactor. The gas mixture was consisted of 10% CO, 20% O_2 and diluted Ar. The total flow rate was kept at 50 ml min^{-1}, corresponding to a gas hourly space velocity (GHSV) of 15,000 ml h^{-1} g^{-1}. And the contact time was 1.2 s. The catalyst was heated to the desired temperatures at a rate of 10 °C min^{-1}, and then kept for 30 min until the catalytic reaction reached a steady state. The reaction products were analyzed using an on-line gas chromatograph (SP-6800A6) equipped with a TCD detector. The CO conversion (X_{CO}) was calculated as follows:

$$X_{CO} = \frac{[CO]_{in}vol\% - [CO]_{out}vol\%}{[CO]_{in}vol\% + \delta[CO]_{out}vol\%} \qquad (1)$$

where $[CO]_{in}$ and $[CO]_{out}$ are the CO concentrations in the inlet and outlet gas, respectively. δ is the expansion factor, and the value is −0.5.