Fuel 229 (2018) 217–226

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

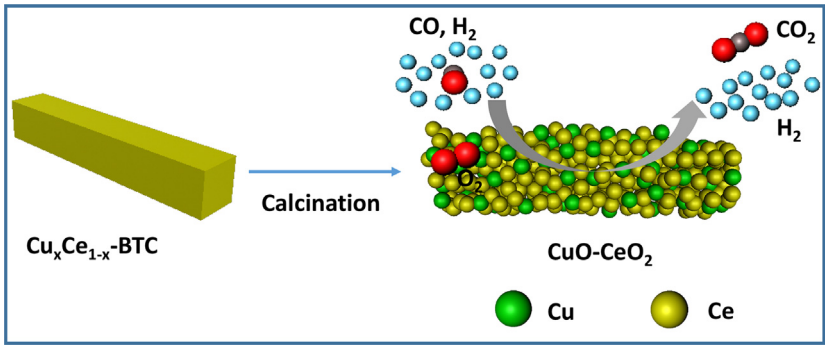
Metal-organic-framework derived controllable synthesis of mesoporous copper-cerium oxide composite catalysts for the preferential oxidation of carbon monoxide

Xia Gong[a], Wei-Wei Wang[c], Xin-Pu Fu[c], Shuai Wei[c], Wen-Zhu Yu[c], Baocang Liu[a,b], Chun-Jiang Jia[c,*], Jun Zhang[a,b,*]

[a] College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, PR China
[b] Inner Mongolia Key Lab of Nanoscience and Nanotechnology, Inner Mongolia University, Hohhot 010021, PR China
[c] Key Laboratory for Colloid and Interface Chemistry, Key Laboratory of Special Aggregated Materials, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China

GRAPHICAL ABSTRACT

A facile MOFs-derived controllable strategy was developed to construct highly active $Cu_xCe_{1-x}O_2$ catalysts through directly annealing Cu_xCe_{1-x}-BTC MOFs under different temperatures for CO-PROX reaction.



ARTICLE INFO

Keywords:
Metal-organic-frameworks
Surface active species
Copper-cerium oxide composite
CO-PROX

ABSTRACT

Among currently studied catalysts, CuO-CeO_2 based materials hold the greatest promise for the preferential oxidation of CO (CO-PROX). Recently, many efforts have been concentrated on developing the original nanostructures inherited from metal-organic-frameworks (MOFs), which are considered to be excellent sacrificial templates or precursors to achieve metal oxide (or metal) nanoparticles with unique structure. In this paper, we synthesized CuO-CeO_2 catalysts using an efficient and general strategy derived from Cu_xCe_{1-x}-BTC MOFs after high temperature treatment. The as-prepared CuO-CeO_2 catalysts display variable morphologies, crystal structures, and specific surface areas based on different ratios of Cu/Ce and calcination temperature. The catalytic performance shows that all CuO-CeO_2 composite catalysts derived from the Cu_xCe_{1-x}-BTC MOFs via heat treatment exhibit excellent catalytic performance for the CO-PROX reaction, and the $Cu_{0.3}Ce_{0.7}O_2$ is the most active catalyst obtained under high calcination temperature at 650 °C for 4 h, demonstrating that the increase of Cu content and high temperature treatment can create more highly dispersed CuO clusters, which is in favor of

* Corresponding authors at: College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, PR China (J. Zhang).
E-mail addresses: jiacj@sdu.edu.cn (C.-J. Jia), cejzhang@imu.edu.cn (J. Zhang).

https://doi.org/10.1016/j.fuel.2018.04.071
Received 15 January 2018; Received in revised form 20 March 2018; Accepted 14 April 2018

the CO-PROX reaction. Meanwhile, the *in-situ* DRIFTS results show that the $Cu_{0.3}Ce_{0.7}O_2$ catalyst displays the super CO adsorption capability, which induces the difference of catalytic performance for the CO-PROX reaction.

1. Introduction

Cerium dioxide (CeO_2) is often used to support transition or noble metals and provides distinctive catalytic functionality due to its typical capacity of shifting between Ce^{4+} and Ce^{3+} and the production of oxygen vacancy defects simultaneously, which are considered to be critical factors for its application in heterogeneous catalysis [1–4]. As we all know that the catalytic activity can be dramatically increased with Au and Pt species supported on CeO_2 for preferential oxidation of CO (CO-PROX), water-gas shift, CO oxidation and oxidation of toluene [5–7]. However, the high cost, poor durability, and low resistance to toxicity of Au and Pt species significantly hinder its large-scale commercial application. In recent years, the development of non-noble metal catalysts with excellent performance has received extensive attention. Among the reported non-noble metal catalysts for various catalytic reactions, ceria-supported CuO catalysts have been regarded as promising candidates due to their low cost, environmental friendliness, and outstanding thermal stability. Landi et al. synthesized CeO_2/CuO wash coated monoliths catalysts by a modified dip coating procedure [8], which presented a good catalytic performance for the CO–PROX reaction. Guo et al. prepared CuO/CeO_2 catalysts via an ethanol-thermal method for the CO-PROX reaction and the catalysts exhibited the excellent catalytic performance. Meanwhile, they investigated the synergistic effect between copper and ceria [9].

Metal–organic frameworks (MOFs) are constituted by the self-assembly of inorganic metal and organic linkers and have drawn much attention in recent years [10–12]. To date, thousands of MOFs and their diverse assemblies formed by a large variety of metal ions and organic linkers have been reported and their structures are not only abundant and intriguing but also designable and tailorable.[13–15]. In addition to their diverse structures and compositions, MOFs possess high surface area, uniform and tunable porosity, and multi-functionality compared with traditional microporous and mesoporous materials. These attractive features make MOFs very promising to be used as precursors and templates for synthesizing hierarchical porous materials for many applications in electrocatalytic oxygen reduction reaction (ORR) [16], Fischer–Tropsch reaction [17], and CO oxidation [18]. Maiti et al. reported a facile method to prepare the nanostructured CeO_2 using [Ce(1,3,5-BTC)$(H_2O)_6$] MOFs as a precursor [19]. Zhang et al. synthesized an efficient CuO/Cu_2O catalyst with specific morphology, crystalline phase, and composition derived from Cu–BTC MOFs [20], which exhibited a high performance for CO oxidation.

In this work, we constructed a series of surface state-finely controlled CuO-CeO_2 catalysts using Cu_xCe_{1-x}-BTC MOFs (BTC = 1,3,5-benzenetricarboxylic acid) as precursors. The interface of CuO-CeO_2 catalysts is maximized by using MOFs as templates, which is in favor of enhancing the catalytic performance for CuO-CeO_2 catalysts [21]. The porous structured CuO-CeO_2 catalysts composed of uniformly dispersed CuO and CeO_2 nanoparticles are achieved by thermolysis of Cu_xCe_{1-x}-BTC MOFs. The synthetic approach is surfactant-free and scalable at a low cost. The optimum porous structured $Cu_{0.3}Ce_{0.7}O_2$ catalysts show favorable catalytic performance for the CO-PROX reaction. Through calcining the $Cu_{0.3}Ce_{0.7}$-BTC MOFs precursor under different temperatures from 450 °C to 750 °C, the optimum $Cu_{0.3}Ce_{0.7}O_2$-650 catalyst with the highest CO conversion (85% at 80 °C) for the CO-PROX reaction can be obtained. The H_2-TPR, Raman, and *in situ* DRIFTS results suggest that the reducibility, oxygen vacancy, and Cu^+ active site of CuO-CeO_2 catalysts have greatly influence on the catalytic performance for CO-PROX reaction.

2. Experimental section

2.1. Preparation of CuO-CeO_2 catalysts

A low temperature solvothermal method was used to synthesize Cu_xCe_{1-x}-BTC frameworks. Briefly, 2 mmol of $Cu(NO_3)_2{\cdot}3H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ were added into 8 mL of deionized water and 12 mL of ethanol. Then, 2 mmol of benzene-1,3,5-tricarboxylic acid (H_3BTC) were added into 12 mL of dimethylformamide (DMF) and subsequently poured into the above mixed solution, continuously stirred for several minutes to form the uniform solution. Then, the mixed solution was transferred into stainless steel reactor with a polytetrafluoroethylene liner at 80 °C for 24 h. Finally, the precipitate was collected and washed using ethanol and DMF, and then dried under oven for 3 days at 130 °C. The powder was calcined at 550 °C for 4 h to obtain CuO-CeO_2 catalysts.

2.2. Characterization of CuO-CeO_2 catalyst

The nitrogen adsorption-desorption test was carried out by a Builder SSA-4200 instrument. XRD was performed on a PANalytical X'Pert3 diffractometer. Raman spectra were measured by Raman microscope system. XPS measurements were finished using VG Scientific ESCALAB Mark II spectrometer. H_2-TPR was performed in a Builder PCSA-1000 instrument. N_2O chemisorption was performed to determine the dispersion of CuO for CuO-CeO_2 samples. (The detail information was listed in Supporting Information)

The *in-situ* DRIFTS experiments were carried out using a Bruker Vertex 70 FT-IR spectrometer. "CO adsorption" experiment was performed to investigate the process of CO adsorption over CuO-CeO_2 catalysts. Prior to experiment, the catalysts (10 mg) were activated by *in situ* calcination at 300 °C for 30 min under synthetic air and then cooled to a certain temperature (80 °C) under pure N_2 (30 mL·min^{-1}). Then the background spectrum was collected via 32 scans at 4 cm^{-1} resolution. Finally, the catalyst was exposed to the feed gas (1% CO + 20% O_2 in N_2) inside the DRIFTS cell, and then the DRIFTS spectra were continuously collected for 30 min at 80 °C. DRIFT spectra were collected by using OPUS software.

2.3. Catalytic tests of CuO-CeO_2 catalysts

The catalytic tests were performed in a plug-flow reactor under the CO PROX reaction. Then, the catalyst (50 mg) was loaded into the reactor under the feed stream (1.0% CO, 1.0% O_2 and 50% H_2 (N_2 balanced)) with the gas flow rate of 50 mL min^{-1}. The catalyst was pretreated under synthetic air (21% O_2/79% N_2) at 300 °C for 30 min for activation. The compositions of the effluent streams were analyzed employing an online gas chromatograph (GC9160 series) with a thermal conductivity detector (TCD) and the sensitivity for CO is about 3840 mV·mL/mg. The CO conversion and CO_2 selectivity were calculated according to the following equations:

$$\text{CO conversion}(\%):\ C_{CO} = (n_{CO,in} - n_{CO,out})/n_{CO,in} \times 100$$

$$\text{CO}_2\text{ selectivity}(\%):\ S_{CO2} = 1/2 \times (n_{CO,in} - n_{CO,out})/(n_{O2,in} - n_{O2,out}) \times 100$$

where $n_{CO,}$ and $n_{O2,}$ are represented peak area values of GC response CO and O_2, respectively, before and after reaction.