



Effect of strongly bound copper species in copper–ceria catalyst for preferential oxidation of carbon monoxide

Pei-Pei Du^a, Wei-Wei Wang^b, Chun-Jiang Jia^{b,*}, Qi-Sheng Song^b, Yu-Ying Huang^a, Rui Si^{a,*}

^a Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China

^b Key Laboratory for Colloid and Interface Chemistry, Key Laboratory of Special Aggregated Materials, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

ARTICLE INFO

Article history:

Received 18 July 2015

Received in revised form

22 September 2015

Accepted 26 October 2015

Available online 31 October 2015

Keywords:

Copper–ceria

Preferential oxidation of carbon monoxide

Ammonium carbonate leaching

X-ray absorption fine structure

Coprecipitation

ABSTRACT

Copper–ceria catalysts with the Cu contents up to 40 at.% were prepared by the coprecipitation method. Ammonium carbonate was used as the leaching agent on the as-calcined samples to remove the weakly bound copper species. The parent and leached catalysts were tested for the preferential oxidation of carbon monoxide (CO-PROX) reaction from 40 to 200 °C in 1%CO/1%O₂/50%H₂/N₂ with a space velocity of 60,000 mL h⁻¹ g_{cat}⁻¹. When the Cu doping amount reached 30 at.%, the stable and constant CO-PROX reactivity, including CO conversion and O₂ selectivity, was presented for both parent and ammonium carbonate leached catalysts. The fresh and used samples have been carefully characterized by various techniques such as power X-ray diffraction (XRD), X-ray absorption fine structure (XAFS), transmission electron microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS) and temperature-programmed reduction by hydrogen (H₂-TPR). It was confirmed that there are two different types of copper species, i.e. weakly bound CuO_x clusters and strongly bound Cu–[O_x]-Ce structure, in both parent and leached catalysts. Furthermore, we have demonstrated that the weakly bound CuO_x clusters removed by ammonium carbonate can be recovered by the migration of Cu–[O_x]-Ce species under the reduction or reaction conditions. The strongly bound copper species in CeO₂ have been identified to be the reservoir for the active Cu sites for CO-PROX.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Currently, clean and efficient energy has been attracted much interest in catalysis. Hydrogen (H₂) in the polymer exchange membrane fuel cells (PEMFCs) has been considered as a good candidate for new energy source. However, a small amount (0.3–1%) of carbon monoxide (CO) remained in the H₂ inlets is severely poisonous to the platinum catalyst used for the electrode materials in PEMFCs [1–3]. Technically, the preferential oxidation of carbon monoxide (CO-PROX) reaction is required to eliminate the toxic CO gas in the hydrogen source after the water–gas shift (WGS) step [4–7]. Besides the diverse noble metal catalysts such as Pt [8–10], Au [11–13], Ru [3], ceria (CeO₂) supported copper oxide (CuO) has been selected for CO-PROX [14–16], because of its high reactivity on both CO conversion and O₂ selectivity, as well as the much lower cost than the noble metal catalysts [17–19].

Various solution-based preparation methods including incipient wetness impregnation [20,21], coprecipitation [20,22] and deposition–precipitation [13,23] have been investigated for the copper–ceria catalysts, leading to the different structural and textural properties in the Cu–Ce–O system. The as-prepared copper oxide phase was either dispersed onto the surface of CeO₂ support [16,21,24], or the Cu²⁺ ions were fully or partially (dependent upon the copper amount) doped into the ceria lattice to substitute the Ce⁴⁺ sites [21,23]. On the other hand, to understand the effects of different types of copper species in ceria, some chemical routes, e.g. the use of leaching agent (cyanide [25], sodium hydroxide [26], sulfuric acid [27] or ammonium carbonate [23]), have been widely used to obtain the leached samples and compared the related results of structural characterization and catalytic test to their parent catalysts.

Meanwhile, multiple characterization skills such as X-ray diffraction (XRD) [28,29], X-ray absorption fine structure (XAFS) [30,31], transmission electron microscope (TEM) [32,33], X-ray photoelectron spectroscopy (XPS) [13,24], and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) [34], have

* Corresponding authors.

E-mail addresses: jjacj@sdu.edu.cn (C.-J. Jia), sirui@sinap.ac.cn (R. Si).

been extensively applied to the copper–ceria catalysts, either before/after the reaction, or in-situ under the CO-PROX working conditions. By the help of these advanced techniques, the bulk and surface structures of copper on ceria ($\text{CuO}_x/\text{CeO}_2$) or copper-doped ceria ($\text{Ce}_{1-x}\text{Cu}_x\text{O}_{2-y}$) have been discovered and correlated to the corresponding reactivity for the studied reactions. These techniques are very helpful to determine the active sites and reaction mechanisms for the copper–ceria CO-PROX catalysts. Among them, XAFS, an elemental-sensitive means, is unique to bypass other effects from the ceria support and extract the structural information on the specific Cu sites. XAFS includes two spectrum ranges, i.e. X-ray absorption near edge spectroscopy (XANES) for electronic structure (oxidation state of $\text{Cu}^0/\text{Cu}^+/\text{Cu}^{2+}$ and charge transfer between metal–metal or metal–oxygen atoms) [34] and extended X-ray absorption fine structure (EXAFS) for short-range (<6–8 Å) local structure (coordination number, bond distance and D.W. factor of Cu–O and Cu–Cu/Ce shells) [35,36].

Furthermore, according to the previous findings on the reducibility of copper–ceria catalyst, the related oxidized copper species synthesized by different methods (coprecipitation, deposition–precipitation, etc.) usually include multiple structures, such as isolated CuO particles, weakly bound CuO_x clusters, strongly bound Cu–[O_x]-Ce and Cu^{2+} ion in the CeO_2 lattice [37]. By the in-situ XAFS measurements, we have previously demonstrated that the weakly bound CuO_x clusters are active species for the CO-PROX reaction [38]. However, the effect of strongly bound copper species is unknown, the contribution of which to the CO-PROX reactivity is still to be explored.

Therefore, in this work, we tried to distinguish the contributions of the above different types of copper species for CO-PROX, with the aid of ammonium carbonate leaching process, which effectively removes the weakly bound CuO_x clusters from the doped CeO_2 surface. In experiments, both parent and leached samples have been tested under the CO-PROX reaction conditions in the temperature range 40–200 °C, and further characterized by XRD, XAFS, TEM, XPS and H_2 -TPR, either before or after the catalytic tests. Based on the results of structural characterization and catalytic tests, we confirmed that the strongly bound Cu–[O_x]-Ce species in CeO_2 can act as the reservoir for the active sites for CO-PROX through the migration onto the surface of the catalyst.

2. Experimental

2.1. Catalyst synthesis

All the chemicals used in this work were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. without any further purification.

The copper–ceria catalysts with different Cu contents were prepared by the coprecipitation method accordingly to the following procedures: (1) $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with a total metal amount of 50 mmol were dissolved in 35 mL Millipore water (18.25 M Ω) and stirred for 15 min at room temperature to form stock solution; (2) The above stock solution was controllably injected into 35 mL NaOH (0.5 mol/L) solution under vigorously stirring with a constant rate of 0.2 mL/min by a mechanically pumping syringe system; (3) After the generation of greenish slurries, the stock solution was further aged at 80 °C for 4 h; (4) The as-obtained precipitates were filtered and washed by Millipore water until the final pH value reached 7.0 approximately. Then, the as-washed product was dried in vacuum at 80 °C overnight, and then air-calcined at 500 °C for 4 h with a ramping rate of 2 °C/min. In this work, the copper–ceria samples were denoted as $x\text{Cu}$ ($x=5, 15, 30$ and 40), where x is the copper content in atomic percent ($x = [\text{Cu}/(\text{Cu} + \text{Ce})] \times 100 \text{ at.}\%$).

For the leaching process, 1.0 g of the parent copper–ceria catalysts after air-calcination were washed by 50 mL ammonium carbonate $[(\text{NH}_4)_2\text{CO}_3, 1 \text{ mol/L}]$ aqueous solution for 4 h at room-temperature under stirring. Then, the as-leached solids were acquired by the sequential filtration, water-washing (pH 7), drying (vacuum, 80 °C, overnight), and air-calcination (300 °C for 4 h, 2 °C/min) steps. The ammonia leached samples were denoted as $x\text{Cu-L}$ ($x=5, 15, 30$ and 40).

2.2. Characterizations

The copper loading concentrations (Cu_{bulk} in at.%) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation).

The powder X-ray diffraction (XRD) patterns were recorded on a Burker D8 Advance diffractometer (40 kV, 40 mA) with a scanning rate of 4° min^{-1} , using Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). The corresponding XRD patterns were collected from 20 to 70° with a step of 0.02° . The 2θ angles were calibrated with a μm -scale Alumina disk. The powder catalyst after grinding was placed inside a quartz-glass sample holder for each test. With the software “LAPOD” of least-squares refinement of cell dimensions from powder data by Cohen’s Method [39,40].

The nitrogen adsorption–desorption measurements were performed on a Builder SSA-4200 unit instrument at 77 K. All the copper–ceria samples were degassed at 150 °C under vacuum for over 6 h. The BET specific surface areas (S_{BET}) were calculated from the adsorption data in the relative pressure range between 0.05 and 0.20.

The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) experiments were carried out on a Philips Tecnai G² F20 instrument at 200 kV. All the tested samples were sonicated in ethanol about 10 min, and then a drop of this dispersed suspension was placed on an ultra-thin (3–5 nm in thickness) carbon film-coated Mo grid. The as-formed sample grid was dried naturally under ambient conditions before inserted into the sample holder. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) mode with energy dispersive spectroscopy (EDS) was applied for the corresponding elemental mapping to obtain the spatial distribution of Cu and Ce in microdomain.

The X-ray absorption fine structure (XAFS) spectra at Cu K-edge ($E_0 = 8979 \text{ eV}$) were performed at BL14W1 beam line of Shanghai Synchrotron Radiation Facility (SSRF) operated at 3.5 GeV under “top-up” mode with a constant current of 240 mA. The XAFS data were recorded under transmission mode for high Cu concentrations (30–40 at.%) with high-flux ion chambers or fluorescence mode for low Cu concentrations (5–15 at.%) with standard Lytle ion chamber, respectively. The energy was calibrated accordingly to the absorption edge of pure Cu foil. Athena and Artemis codes were used to extract the data and fit the profiles. For the X-ray absorption near edge structure (XANES) part, the experimental absorption coefficients as function of energies $\mu(E)$ were processed by background subtraction and normalization procedures, and reported as “normalized absorption”. Based on the normalized XANES profiles, the molar fraction of $\text{Cu}^{2+}/\text{Cu}^+/\text{Cu}^0$ can be determined by the linear combination fit [38,41]. For the extended X-ray absorption fine structure (EXAFS) part, the Fourier transformed (FT) data in R space were analyzed by applying 1st shell approximation or metallic Cu model for the Cu–O or Cu–Cu shell, respectively. The passive electron factors, S_0^2 , were determined by fitting the experimental Cu foil data and fixing the Cu–Cu coordination number (CN) to be 12, and then fixed for further analysis of the measured samples. The parameters describing the electronic properties (e.g., correction to the photoelectron energy origin, E_0) and local structure environ-

Download English Version:

<https://daneshyari.com/en/article/38992>

Download Persian Version:

<https://daneshyari.com/article/38992>

[Daneshyari.com](https://daneshyari.com)