Applied Catalysis B: Environmental 146 (2014) 201–212

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Efficient fabrication of active CuO-CeO$_2$/SBA-15 catalysts for preferential oxidation of CO by solid state impregnation

Changjin Tang[a], Jingfang Sun[a], Xiaojiang Yao[a], Yuan Cao[a], Lichen Liu[a], Chengyan Ge[a], Fei Gao[b,*], Lin Dong[a,b,*]

[a] Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China
[b] Jiangsu Key Laboratory of Emission Control, Center of Modern Analysis, Nanjing University, Nanjing 210093, PR China

ARTICLE INFO

Article history:
Received 24 September 2012
Received in revised form 25 April 2013
Accepted 23 May 2013
Available online 30 May 2013

Keywords:
Solid state impregnation
CuO-CeO$_2$
Interfacial interaction
CO-PROX
CO adsorption

ABSTRACT

A facile solid state impregnation method was reported to prepare CuO-CeO$_2$/SBA-15 catalysts for preferential oxidation of CO (CO-PROX). The catalysts were studied and compared with the counterpart from traditional wet impregnation. All catalysts together with a bulk CuO-CeO$_2$ were characterized by XRD, N$_2$ sorption, TEM, XPS, FT-IR of CO adsorption and H$_2$-TPR. Results showed that: (1) both copper and ceria were well dispersed on SBA-15, and by adoption of a supported CuO-CeO$_2$ configuration, the CO-PROX activities were greatly enhanced, which could be attributed to the distinct reduction of ceria size; (2) the optimum copper loading was 5 wt%, and obvious decrease of CO$_2$ selectivity was observed at higher loading; (3) in comparison with wet impregnation, the solid state impregnation displayed advantages of increased interfacial CuO-CeO$_2$ entities and enhanced interaction between CuO and CeO$_2$, which increased the active site and upgraded the CO-PROX activity resultantly. As well, the reason accounting for the different properties was tentatively discussed. On the basis of the preliminary results, it is supposed the solid state impregnation will find unique application in fabrication of multi-component heterogeneous catalysts.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Preferential oxidation of CO (CO-PROX) has attracted numerous interests in recent years for its potential of avoiding poisoning of Pt-based anode in proton exchange membrane fuel cell (PEMFC) [1,2]. The key requirements for CO-PROX catalysts include extremely high CO oxidation activity, high selectivity, and wide operation window [3]. Supported Au and Pt catalysts are active for CO-PROX reaction, but they suffer from such drawbacks as high cost, limited availability and relatively low selectivity at high temperatures. Therefore, the development of non-precious catalysts with favorable performance is desirable.

Among the reported non-precious catalysts for CO-PROX, copper-ceria catalysts have gained tremendous attention [4–7]. In general, their activities are correlated with the synergetic effect between copper and ceria [6,8,9], and are intimately influenced by the adopted preparations. Chung and Yeh studied the effect of pH value on CuO/CeO$_2$ catalysts and found precipitation at high pH led to enhanced interaction between copper and ceria, which increased the CO-PROX activity [10]. Lee and co-workers investigated the impact of hydrothermal treatment after co-precipitation procedure on the property of CuO/CeO$_2$ catalyst. They found that under hydrothermal process, cuprous ions would migrate to the surface of the catalyst resulting in increased concentration of interfacial copper-ceria entities. As a consequence, improved CO conversion was obtained [11].

In addition to preparation parameters, the activity of CuO-CeO$_2$ catalysts over CO-PROX is reported to be also affected by their configurations [12]. Commonly, the configurations of CuO-CeO$_2$ catalysts can be classified into three kinds, *i.e.*, CuO/CeO$_2$, inverse CeO$_2$/CuO and supported CuO-CeO$_2$. In contrast to the overwhelming investigations on CuO/CeO$_2$, little attention has been paid to the application of supported CuO-CeO$_2$, despite their favorable performances. Chilukuri and co-workers studied the possibility of using Al-pillared montmorillonite (Al-PILC) clay as a support for CuO-CeO$_2$ catalysts [13] and result showed that the CuO-CeO$_2$/Al-PILC catalysts were comparable to supported noble metal catalysts in the performance of CO-PROX. Araya and co-workers put their attention on the effect of various supports (Al$_2$O$_3$, ZrO$_2$ and SiO$_2$) on CuO-CeO$_2$ catalysts and pointed out that the employed supports exerted a critical influence on the interaction degree between copper and ceria, and consequently the CO-PROX activity, with CuO-CeO$_2$ supported on SiO$_2$ displaying the best CO oxidation activity [14].

---

* Corresponding authors at: Jiangsu Key Laboratory of Emission Control, Center of Modern Analysis, Nanjing University, Nanjing 210093, PR China.
Tel.: +86 25 83592290; fax: +86 25 83317761.
E-mail addresses: gaofei@nju.edu.cn (F. Gao), donglin@nju.edu.cn (L. Dong).

0926-3373/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2013.05.060

For supported $CuO-CeO_2$ catalysts, the effective interaction between copper and ceria is vital. It is properly supposed that by adopting a suitable method, the interaction between copper and ceria on the third support would be altered, which dictates their final performance. So far, methods for dispersing multiple components onto a support are dominated by wet impregnation, whereas the investigations of other methods are seldom reported and the direct comparison between them is lacking. Recently, a typical method featuring of solid state impregnation was reported by others [15,16] and performed in our laboratory [17], and unique capacity in dispersion was achieved for mono-component species supported on mesoporous SBA-15. Actually, in many catalyst systems, in addition to the support and active component, a promoter or modifier is usually added to obtain certain desirable properties (*e.g.* improved activity, selectivity, thermal stability, and poison resistance). In that case, the interactions between active species, promoter as well as support are complex, and the capacity of solid state impregnation in distributing guest species and modulating their interactions is still a question of great interest. Moreover, because of the complexity of the systems, it is still unclear how copper and ceria interact with each other and how such interaction promotes catalytic activities. Hence, in the present study, as an alternative to wet impregnation, we extend the solid state impregnation to fabricate $CuO-CeO_2$/SBA-15 catalysts. The main focus of the present study is to: (1) investigate the effectiveness of solid state impregnation in preparing SBA-15 supported copper-ceria catalysts; (2) explore the differences in the composition and structure of the catalysts made by solid state impregnation and wet impregnation, and correlate them with the CO-PROX activity. The characterization results reveal that both CuO and CeO_2 are well dispersed and the interaction between copper and ceria can be enhanced *via* the solid state impregnation. As a result, the obtained catalysts display superior performance in CO-PROX, in comparison with bulk $CuO-CeO_2$ and $CuO-CeO_2$/SBA-15 from wet impregnation.

2. Experimental

2.1. Preparation of catalyst

2.1.1. Preparation of SBA-15 supported $CuO-CeO_2$ catalysts by solid state impregnation

All chemicals used in the experiments were of analytical grade, and were used without further purification. Synthesis of SBA-15 follows Zhao's process [18]. The solid state impregnation to $CuO-CeO_2$/SBA-15 catalysts was operated as follows. A certain amount of $Ce(NO_3)_3{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ were added to an agitate mortar with SBA-15 and manually ground for 0.5 h. Then the mixed powder was transferred into a crucible, which was placed in the muffle furnace. The thermal treatment in air started at room temperature with a ramp of 1 °C min^{-1} to 450 °C and maintained at that temperature for 4 h, then cooled naturally. For simplicity, the obtained samples were denoted as *x*CuCe/SBA-15-SSI, where ceria content was set to 20 wt% and *x* represented the weight percentage of CuO to SBA-15. As well, 5Cu/SBA-15-SSI was prepared by the same procedure.

2.1.2. Preparation of SBA-15 supported $CuO-CeO_2$ catalyst by wet impregnation method

The supported $CuO-CeO_2$ catalyst from wet impregnation was prepared by impregnating SBA-15 with an aqueous solution containing requisite amount of $Ce(NO_3)_3{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$. After stirred for 2 h, the sample was dried at 100 °C in oil bath, subsequently dried at 110 °C in an oven overnight, and then calcined in air at 450 °C for 4 h. The obtained catalyst was denoted as 5CuCe/SBA-15-WI, and the copper and ceria contents are identical to that in 5CuCe/SBA-15-SSI.

2.1.3. Preparation of bulk $CuO-CeO_2$ catalyst

As a representative of commonly employed copper-ceria configuration, CuO/CeO_2 catalyst was fabricated for comparison. The nominal ratio of CuO to ceria was set identical to that in 5CuCe/SBA-15-SSI, *i.e.*, $CuO{:}CeO_2 = 1{:}4$ (w/w). The catalyst was prepared by a co-precipitation method and noted as bulk CuCe. Typically, an aqueous solution of NaOH (1 M) was added dropwise to an aqueous mixture solution of cupric nitrate and cerium nitrate under stirring, and the pH of the finally resulted solution was controlled to *ca.* 10. After continued stirring for 3 h followed by aging for another 3 h, the resulted precipitate was filtered, washed with distilled water for several times, and dried at 110 °C overnight. Finally, the precipitate was air-calcined at 450 °C for 4 h.

2.2. Characterization of catalyst

The CuO and ceria contents in $CuO-CeO_2$/SBA-15 catalysts were determined by a Jarrell-Ash 1100 inductively coupling plasma (ICP) atomic emission spectrometer. The samples were completely dissolved in the mixed hot solutions of HF and H_2O_2 before analysis. The actual contents are equal to their nominal loadings.

X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert Pro diffractometer, equipped with a Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). The X-ray tube was operated at 40 kV and 40 mA. The average grain size was determined from XRD line broadening measurement using the Scherrer equation, $d = K\lambda/\beta\cos\theta$, where λ is the X-ray wavelength, θ is the diffraction angle, K is the particle shape factor, usually taken as 0.89, and β is full width at half maximum in radians.

Nitrogen physisorption isotherms were measured at −196 °C using a Micromeritics ASAP 2020 system. The samples were degassed for 160 min at 300 °C in the degas port of the adsorption analyzer. The pore size distributions were calculated from the adsorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) algorithm.

Transmission electron microscopy (TEM) images were taken on a JEM-2100 instrument at an acceleration voltage of 200 kV. The sample was dispersed in A.R. grade ethanol with ultrasonic treatment and the resulting suspension was allowed to dry on carbon film supported on copper grids.

H_2 temperature-programmed reduction (H_2-TPR) measurement was carried out in a quartz U-tube reactor. Before reduction, the samples were pretreated in N_2 stream at 150 °C for 1 h and then cooled to room temperature. After that, a H_2-Ar mixture (7% H_2 by volume) with a flow rate of 70 mL min^{-1} was switched on and the temperature was increased linearly at a rate of 10 °C min^{-1}. A thermal conductivity cell was used to detect the consumption of H_2 on stream.

X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5000 Versaprobe system, using monochromatic Al Kα radiation (1486.6 eV) operating at an accelerating power of 150 W. The samples were outgassed at room temperature in a UHV chamber ($<5 \times 10^{-7}$ Pa). All binding energies (B.E.) were referenced to the C 1s peak at 284.6 eV. The experimental errors were within ±0.1 eV.

FT-IR spectra were collected on a Nicolet 5700 FT-IR spectrometer at a resolution of 4 cm^{-1}. The spectra of empty IR cell were collected in CO atmosphere at various target temperatures as background. The catalysts were mounted in a commercial controlled environment chamber (HTC-3) and pretreated for 1 h at 150 °C in flowing N_2 atmosphere. After cooled to room temperature, the sample wafers were exposed to a controlled stream of CO-Ar (10% of CO by volume) at a rate of 5.0 mL min^{-1} for 30 min. Adsorption studies were performed by heating the adsorbed species and the spectra

Download English Version:

https://daneshyari.com/en/article/45199

Download Persian Version:

https://daneshyari.com/article/45199

Daneshyari.com