Applied Catalysis A: General 502 (2015) 129–137

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

High performance of Cu/CeO_2-Nb_2O_5 catalysts for preferential CO oxidation and total combustion of toluene

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ARTICLE INFO

Article history:
Received 1 April 2015
Received in revised form 20 May 2015
Accepted 29 May 2015
Available online 4 June 2015

Keywords:
Niobium addition
Cuo-ceo$_2$
CO oxidation
Toluene oxidation
Copper catalysts

ABSTRACT

Copper-based catalysts supported on niobium-doped ceria have been prepared and tested in the preferential oxidation of CO in excess of H_2 (PROX) and in total oxidation of toluene. Supports and catalysts have been characterized by several techniques: N_2 adsorption, ICP-OES, XRF, XRD, Raman Spectroscopy, SEM, TEM, H_2-TPR and XPS, and their catalytic performance has been measured in PROX, with an ideal gas mixture (CO, O_2 and H_2) with or without CO_2 and H_2O, and in total oxidation of toluene. The effects of the copper loading and the amount of niobium in the supports have been evaluated. Remarkably, the addition of niobia to the catalysts may improve the catalytic performance in total oxidation of toluene. It allows us to prepare cheaper catalysts (niobia it is far cheaper than ceria) with improved catalytic performance.

1. Introduction

The preferential oxidation of CO in hydrogen-rich gas mixtures (PROX) has gained importance due to its potential application in fuel cell energy systems. On the other hand, volatile organic compounds (VOCs) are toxic and contribute significantly to the formation of the photochemical smog, which has remarkable impact to the air quality; therefore, the research on the removal of VOCs has attracted increasing interests during the last years. In this way, Cu-based catalysts have generated a lot of interest to be used in PROX and VOCs reactions due to their easy availability, low cost and high activity and selectivity [1–3]. In these cases, among the most studied catalysts for these reactions are those based on the CuO_x–CeO_2 system. The advantages to use this type of catalysts are associated with the fact that the presence of copper oxide on ceria could promote the oxygen storage capacity (OSC), the thermal stability of cerium oxide [4,5] and its redox properties (between the metal and the support at interfacial sites [1,6–9]). It means that the redox properties of copper oxide, in general, depend on a more or less extent of its interaction with the cerium oxide.

Furthermore, there are some factors that could influence the catalytic properties of these materials, like: (i) the synthesis method, (ii) the calcination temperature and (iii) the metallic loading [10–12]. In this sense, Liu et al. [11], have investigated the influence of different preparation methods for CuO–CeO_2 catalysts (co-precipitation, quelate effect, citric acid method and critic phase), and the authors observed that the "quelate effect" method offered the best results. This observation could be related with the formation of defects in the cerium oxide and, consequently, with the synergic effect between the Cu(I)/Cu(II) and Ce(III)/Ce(IV). Martínez-Arias et al. [12] suggested a model for the redox process on copper-ceria catalysts. They proposed that the first step involves the reduction of copper oxide, which might occur at interface positions with the support, favoring the reduction of the latter. In this case, the re-oxidation is generally easier. In a second step, the reduction of copper oxide is extended to ceria positions distant from the interface. In this case, the re-oxidation is takes place firstly on the ceria surface situated far from the interface, while copper oxidation happens next, and it is softened a little bit due to the stabilization of a copper reduced state (Cu(I)) during the redox cycle.

One of the main problems of CuO_x/CeO_2 catalysts is the volatile price of ceria. Thus, prices for rare earths had been flat for most of the 1990s into mid-2000s, but then they have increased signif-

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http://dx.doi.org/10.1016/j.apcata.2015.05.033
0926-860X/

icantly from the early 2010s due to a combination of constraints placed on mining, processing and exporting levels by countries producers (mainly China), and a continued strong global demand for ceria products. Ceria reached a peak level in mid-2011 before declining through early 2012. Still, today the price of ceria doubles the price in 2007. It is clear that catalysts having less content in ceria and maintaining or improving their catalytic activity are needed [13].

Niobium oxide is an abudant and cheap oxide that is mainly produced in Brazil, and its production is totally decoupled from the production of rare earths. Furthermore, niobium oxide possesses several properties that make it promising for catalytic applications. Bearing this in mind, niobia based materials are effective catalysts in selective oxidation reactions due to its redox properties [14]. Furthermore, niobia-doped ceria materials have shown a good tolerance to carbon deposition and excellent properties as solid oxide fuel cell (SOFC) anodes [14,15].

Previously, in our work group, we have studied the influence of Nb addition to Pt/CeO_2 catalysts in the PROX reaction [16]. The results have shown that it favors CO oxidation, although the selectivity towards CO_2 was still a little low, about 50%.

With the idea of preparing catalysts with lower cost and higher activity and selectivity, the aim of this work is to study the influence of copper properties and the addition of niobium oxide to cerium oxide support for two important reactions, the preferential CO oxidation reaction in the presence of hydrogen and the total oxidation of toluene as representative of VOCs removal reactions.

2. Experimental Section

2.1. Preparation of ceria and niobium-doped ceria supports

Cerium oxide support was prepared by the homogeneous precipitation method, according with the procedure reported in reference [19]. 13 g of $Ce(NO_3)_3 \cdot 9H_2O$ (Aldrich, 99%) and 8 g of urea (Fluka, 98%) were dissolved in 400 ml of ultra-pure water. The mixture was heated at 363 K with constant stirring for 11 h. Finally, between 12 ammonia solution (Panreac, 30%) was added drop-wise to ensure complete precipitation. The solid was separated by filtration, washed with ultrapure water, and finally dried at 383 K overnight. The power sample was calcined in air at 773 K for 4 h, using a rate of $3\ K{\cdot}min^{-1}$.

A series of niobium-doped ceria supports was prepared following the same process showed above. An appropriate amount of cerium nitrate (Aldrich, 99%) and ammonium niobate (V) oxalate hydrate (Aldrich, 99.99%), together with urea (Fluka, 98%), were dissolved in 400 ml of ultra-pure water to obtain different supports of composition $xCeO_2$-$(1-x)Nb_2O_5$, with $x = 1$, 0.9, 0.7 and 0.4. The mixture was heated at 363 K with constant stirring during 11 h. Finally, ammonia solution (Panreac, 30%) was added dropwise to ensure complete precipitation. The solid was separated by filtration, washed with ultrapure water, and finally dried at 383 K overnight. The power samples were calcined in air at 773 K for 4 h, using a rate of $3\ K \cdot min^{-1}$.

2.2. Preparation of the CuO catalysts

Different $Cu/xCeO_2$-$(1-x)Nb_2O_5$ catalysts were prepared by the wetness impregnation method. The supports, $xCeO_2$-$(1-x)Nb_2O_5$ ($x = 1$, 0.9, 0.7 and 0.4), were impregnated with an aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (Panreac, 99.999%) with the appropriate concentration to achieve 4 and 8 wt.% Cu loading. Then, catalysts were dried at 383 K overnight and calcined in air at 773 K for 4 h, with a heating rate of $3\ K\ min^{-1}$.

2.3. Materials characterization

The textural properties of the supports were characterized by nitrogen adsorption measurements at 77 K, which were performed in a house developed fully automated manometric equipment. Prior to the adsorption experiments, samples were degassed under vacuum (10^{-4} Pa) at 523 K for 4 h. The BET surface area was estimated after application of the BET equation.

The actual metal loading of the different catalysts was determined by ICP in a PerkinElmer device (Optimal 3000). For this purpose, the metal was extracted from the catalysts by refluxing them in aqua regia for 8 h.

XRF patterns were performed on a X-ray sequential spectrometer Philips Magix Pro equipped with a rhodium X-ray tube and beryllium window was used.

X-Ray powder diffraction patterns were recorded on a Bruker D8-Advance with Göebel mirror and a Kristalloflex K 760–80 F X-ray generation system, coupled with a Cu cathode and a Ni filter. Spectra were registered between 20 and 80° (2θ) with a step of 0.05° and a time per step of 3 s.

Temperature-programmed reduction (TPR-H_2) with H_2 measurements were carried out on calcined catalysts in a U-shaped quartz cell using a 5% H_2/He gas flow of $50\ ml\ min^{-1}$, with a heating rate of $10\ K\ min^{-1}$. Samples were treated with flowing He at 423 K for 1 h before the TPR run. Hydrogen consumption was followed by on-line mass spectrometry and calibrated by carrying out the reduction of CuO and assuming that it is completely reduced to metallic copper.

Raman spectra were recorded on a FT-Raman Bruker RFS/100 spectrometer with coupled microscope. Spectra were recorded at room temperature (274 K, 85% relative humidity) between 4000 and $400\ cm^{-1}$ with a spectral resolution of $4\ cm^{-1}$. Raman spectra were obtained using different conditions depending on the type of sample used. In the case of samples with a very intense Raman effect, a laser power of 100 mW and 32 scans was used, whereas for other samples (for example, those with a larger amount of niobium) 200 mW were used and between 128 and 256 scans collected. Calibration was carried out with a silicon single crystal at $520.7 \pm 2\ cm^{-1}$. The frequency of the exciting Raman source was 1064 nm.

TEM images were obtained on a JEOL electron microscope (model JEM-2010) working at 200 kV. It was equipped with an INCA Energy TEM 100 analytical system and a SIS MegaView II camera. Samples for analysis were suspended in ethanol and placed on copper grids with a holey-carbon film support.

SEM micrographs were obtained on a scanning electron microscope Hitachi S3000N, which is equipped with a Bruker XFlash 3001 X-ray detector for microanalysis (EDS) and mapping.

X-ray photoelectron spectroscopy was performed with a K-Alpha spectrometer (Thermo Scientific). All spectra were collected using Al-Kα radiation (1486.6 eV), monochromatized by a twin crystal monochromator, yielding a focused X-ray spot with a diameter of 400 μm, at 3 mA × 12 kV. The alpha hemispherical analyzer was operated in the constant energy mode with survey scan pass energies of 200 eV to measure the whole energy band and 50 eV in a narrow scan to selectively measure the particular elements. Charge compensation was achieved with the system flood gun that provides low energy electrons and low energy argon ions from a single source. The powder samples were pressed into small Inox cylinders, mounted on the sample holder and placed in the vacuum chamber. Before recording the spectrum, the samples were maintained in the analysis chamber until a residual pressure of ca. $5 \times 10^{-7}\ N\ m^{-2}$ was reached. The quantitative analysis were estimated by calculating the integral of each peak, after subtracting the S-shaped background, and by fitting the experimental curve to a combination of Lorentzian (30%) and Gaussian (70%) lines.