Chemical Engineering Journal 160 (2010) 13–19

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Synthesis, characterization, and promoter effect of Cu-Zn/γ-Al_2O_3 catalysts on NO reduction with CO

Hui-Hsin Tseng[a,b,*], Hsiao-Yi Lin[a,b], Yu-Feng Kuo[a,b], Yi-Ting Su[a,b]

[a] *School of Occupational Safety and Health, Chung Shan Medical University, Taichung 402, Taiwan, ROC*
[b] *Department of Occupational Medicine, Chung Shan Medical University Hospital, Taichung 402, Taiwan, ROC*

ARTICLE INFO

Article history:
Received 2 September 2009
Received in revised form 11 February 2010
Accepted 20 February 2010

Keywords:
Polyol method
Bimetallic catalyst
NO reduction
CO oxidation
Promoter

ABSTRACT

The role of the Zn promoter and the preparation route in the catalytic properties of Cu-Zn/γ-Al_2O_3 catalysts towards NO reduction with CO were investigated in this study. The catalysts were prepared by chemical reduction of the corresponding metal species ($Cu(NO_3)_2{\cdot}2.5H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$) by a liquid polyol solution. The nano-bimetallic catalysts were obtained through this method, in which heterogeneous nucleation by seeding the reactive medium with foreign nuclei, Cu, was synthesized by the addition of an easier reductive metallic precursor to replace the homogeneous nucleation. Several samples were prepared with a variation in the reduction temperature, reduction time, Cu/Zn atomic ratio, and Cu and/or Zn loading weight in the catalysts. The morphology and surface chemical structure of the samples were assessed by transmission electron microscopy (TEM), BET surface area measurements, and X-ray photoelectron spectroscopy (XPS). Based on TEM evidence, the Cu-Zn/γ-Al_2O_3 catalysts were found to be composed of a spherical Cu-Zn nanoparticle, and the particle size decreased with the addition of Zn. XPS was used to study the different chemical states of the Zn-promoted Cu/γ-Al_2O_3, which indicated that the concentration of the reduced Cu species was related to the addition of Zn, thus increasing the NO conversion. The results obtained suggest that the use of Zn as a promoter and the polyol method as a preparation route played important roles in the properties of the catalysts, the Cu particle size, the reduction/oxidation efficiency of Cu/Zn, and the catalytic properties of NO reduction with CO.

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1. Introduction

The selective catalytic reduction (SCR) of NO in the presence of oxygen with hydrocarbons [1–5] has been considered as a promising method for NO reduction due to its significant environmental impact. Among the different catalysts and active phase formulations that have been proposed for this reaction, Cu-based transition metal catalysts have been widely known for their SCR-CxHy reaction ever since Bethke et al. [2] found that Cu/γ-Al_2O_3 is highly active for the reduction of NO with C_3H_6 at a temperature of 315 °C. For this reaction, the activity is generally proportional to the Cu surface area, the dispersion, and the concentration of the oxidation state of Cu, Cu_2O, and CuO. Pillai and Deevi [6,7] also indicated that the rate-determining step for this reaction is related to in the oxidation state of Cu.

From a theoretical standpoint, the oxidation state of Cu-based catalysts can be modified through the multiple functions of the promoters or via the different preparation routes. For the former, various oxides and their mixtures have been used as a promoter for Cu, mostly ZnO and CeO_2 [8–10]. ZnO is known to improve both the dispersion of Cu and the reducibility of CuO, which have been cited as the possible reasons for the activity of Cu/ZnO catalysts if a Cu redox step occurs in the mechanism. However, it is also possible that improved adsorption can cause better activity. The adsorption properties of Cu/ZnO can affect activity because Zn can promote the formation of a linear or weakly bonded CO on the surface of Cu/ZnO [6]. Varying the synthesis routes also leads to changes in morphology, dispersion, and Cu species. Current preparation methods for SCR catalysts include the impregnation method [4,11], the ion exchange method [12], and the surfactant-templated method [8]. In the present work, the polyol method is used to synthesize Cu-Zn/γ-Al_2O_3, which was likewise employed for the preparation of nano-scaled photocatalysts in our previous study [13].

The polyol process is a kind of alcohol reduction method [14] known to be a chemical reduction agent-free method. In this process, a liquid polyol such as 1,2-ethanediol or 1,3-propanediol acts both as a solvent and as a mild reducing agent. The metal ions are mainly reduced by redox reaction between the metallic precursor and the solvent. The reaction mechanism has been investigated by Larcher and Patrice [15]. For the reduction of $Ni(OH)_2$ or $Co(OH)_2$

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[*] Corresponding author at: School of Occupational Safety and Health, Chung Shan Medical University, Taichung 402, Taiwan, ROC. Tel.: +886 4 24730022x11823; fax: +886 4 23248194.
E-mail address: hhtseng@csmu.edu.tw (H.-H. Tseng).

1385-8947/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.cej.2010.02.039

into metallic Ni or Co by ethylene glycol (EG), they found that the degradation of EG takes place in two steps. The first step is the dehydration of EG which gives rise to acetaldehyde, and the second is the duplicative oxidation of acetaldehyde with the formation of diacetyl [Eq. (1)]:

$$2CH_2OH\text{-}CH_2OH \rightarrow 2CH_3CHO + 2H_2O \quad (1)$$

This transformation was found to take place at the same time as the formation of metallic powder [Eq. (2)]:

$$2CH_3CHO + M(OH)_2 \rightarrow CH_3COCOCH_3 + 2H_2O + M^0\,(M = CoorNi) \quad (2)$$

In this process, nucleation and growth must be two completely separate steps to obtain monodisperse particles. It is well established that the concentration of the solute in the solution will affect the nucleation and growth rate, while the concentration reaches the critical supersaturation level when the spontaneous nucleation step begins. After the nucleation lowers the solute concentration below the self-nucleation level, the nucleation stage becomes short and is followed by the growth of the particles from the original nuclei for as long as the solute is slowly generated [16]. To decrease the solute generation rate and prevent the coagulation of particles during their growth stage, a dilute solution is used, or the pH of the solution is adjusted in order to increase the electrical repulsion between particles [17]. In some cases, protective agents such as PVP are also used to produce steric stabilization [18].

In the present study, the heterogeneous nucleation by seeding a reactive medium with a foreign nuclei, Cu, is synthesized by adding a more reductive metallic precursor $Cu(NO_3)_2$ to replace the homogeneous nucleation. Furthermore, to speed up the reduction of Cu(II) by EG, the reduction temperature needs to be increased, but it may exhibit a high degree of particle sintering. It is therefore necessary to restrain the temperature under appropriate conditions. To our knowledge, however, no reports on the polyol synthesis of Zn-promoted Cu/Al_2O_3 materials have been published to date.

As compared to the NH_3 reducing agent, CO was found to have lower reactivity towards NO [19–21] under low reaction temperature. In this paper, a series of nanosized Cu/Zn catalysts with different oxidation states was prepared by a polyol method under various conditions such as reduction temperature, reduction time, and Cu/Zn atomic ratio. Their catalytic performance towards NO reduction by CO was also investigated.

2. Experimental

2.1. Materials

Alumina (γ-Al_2O_3) supplied by Alfa-Aesar was used as the catalyst support throughout this work. Its main physical data are as follows: Brunauer–Emmett–Teller (BET) surface area (S_{BET}) 362.3 m^2/g, average pore size around 76.98 Å, and purity above 98%. Copper nitrate [$Cu(NO_3)_2 \cdot 2.5H_2O$] (Aldrich) and zinc nitrate [$Zn(NO_3)_2 \cdot 6H_2O$] (Aldrich) were used as the precursors corresponding to each catalyst. EG was used to reduce the metallic ions. Polyvinylpyrrolidone (PVP) (Sigma–Aldrich, molecular weight = 10000 g mol^{-1}) was used as a nucleation-protective agent to avoid nanoparticle sintering and aggregation.

2.2. Catalyst preparation

The supported mono-metallic Cu and bimetallic Cu/Zn catalysts were prepared as follows. The proper amounts of the precursors corresponding to the desired Cu/γ-Al_2O_3 or Cu-Zn/γ-Al_2O_3 weight ratio (Cu metal loading: 3 wt.%, ratio of Zn/Cu = 0.3, 0.5, 0.75 and 1 in atomic ratio) and 0.5 g of PVP were completely dissolved in EG-γ-Al_2O_3 solution. The reduction of the metallic ion was then produced by heating the mixed polyol solution up to the desired temperature (50–170 °C) at a rate of 5 °C min^{-1}, and this was kept for 0–60 min to react. At the end of the reaction time, the solution was rapidly cooled to 0 °C through an ice bath. Following filtration and washing, the resulting product was dried at 105 °C overnight and calcined in air at 400 °C for 4 h to remove the carbonate and crystal water which remaining on the surface of catalysts. Henceforth, they are abbreviated to CuZnx/γ-Al_2O_3-Y-Z (X, Y, and Z denote the Zn/Cu atomic ratio, reaction temperature, and reaction time, respectively).

2.3. Catalyst characterization

After calcination, the samples were characterized by flame atomic absorption spectroscopy (FAAS), BET, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The metal content in the catalysts was determined by FAAS. Before measuring, the samples were dissolved in dilute HNO_3-HF mixed solution by microwave digestion. The textural properties of the samples were measured by N_2 sorption at −196 °C with a PMI Automated BET Sorptometer (201AEL). TEM measurements were carried out with a JEOL 100CXII operating at 200 kV. During the preparation, the suspension was deposited on a Cu grid coated with a porous carbon film. XPS measurements were carried out on a PHI 5000 VersaProbe/Scanning ESCA Microprobe (ULVAC-PHI). All binding energies were corrected using a C 1s photoelectron peak at 284.6 eV as reference. The full widths of the peak at half maximum were allowed to adjust in order to attain the best fitting.

2.4. Catalytic tests

The catalytic activity of Cu/γ-Al_2O_3 or the Cu-Zn/γ-Al_2O_3 catalysts for the CO-SCR process was carried out in a continuous flow system with a fixed bed quartz reactor (15 mm I.D.) at atmospheric pressure. The experimental equipment consists of three sections: the gas feeding system, the reactor, and the gas analyzer. The catalysts were loaded with the aid of quartz wool and heated to the desired reaction temperature using an electric heater with PID controllers. Based on the stoichiometry (λ) of CO-SCR reaction ($2NO + CO \rightarrow N_2 + CO_2 + 1/2O_2$), we defined the λ as the ration of [NO]/[CO] ([NO]: concentration of NO; [CO]: concentration of CO) and discussed the effect of λ ($\lambda = 1$ and 2) on the NO conversion. Reagent gas mixtures containing NO, CO, 6% of O_2, and He as balance gas were adjusted by mass flow controllers (Brooks, 5850E). The corrosion resistant flow controllers were purged with high purity He between experiments. The total flow rate was 650 ml min^{-1}, which could be converted to a GHSV of $2.4 \times 10^4\ h^{-1}$, and the use of support particles size with a diameter range of 125–177 μm indicated that the mass and heat transfer limitations could be considered negligible by the calculation of effectiveness factors in our experimental conditions. Prior to the catalytic reaction, the catalysts were heated at the proper temperature in a He flow for 2 h. The catalytic activity was examined over a range of temperature (200–250 °C). After reaching the reaction temperature, the He gas flow was switched to the reactant feed gas flow. In all cases, the reaction was continued until the outlet stream concentration changed by less than 2%, at which time steady state conditions were assumed.

Concentrations of CO, CO_2, and NO were continuously measured by an online non-dispersive infrared gas analyzer (HORIBA PG-250A). The catalytic activity was evaluated in terms of NO conversion to N_2 and CO conversion to CO_2. The formation of NO_2 and N_2O analyzed by gas chromatograph with a thermal conductivity detector was found to be negligible in the present work because the selectivity of NO to N_2 was higher than 98% in all experiments.

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