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Catalytic activity of Au-Cu/CeO_2-ZrO_2 catalysts in steam reforming of methanol

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ABSTRACT

Bimetallic Au-Cu/$Ce_{0.75}Zr_{0.25}O_2$ catalysts prepared by deposition–precipitation were tested for steam reforming of methanol (SRM) in the range of 200–500 °C. Many effective parameters—Au/Cu atomic ratio, gas pretreatment, total metal loading, and calcination temperature—were investigated and correlated with catalyst properties. At the Au/Cu ratio of 1/3, the homogeneous Au–Cu alloy was found to be active for SRM, while an inhomogeneous or partially developed alloy formation was found after applying H_2 and O_2 pretreatments. There were no significant differences in catalytic activity with different total loadings and calcination temperatures; however, the 7 wt% Au-Cu catalyst calcined at 300 °C exhibited complete methanol conversion, 82% H_2 selectivity, and 1% CO selectivity at a low temperature of 300 °C. In regards to stability, the bimetallic catalyst displayed a long life, even though coke and metallic copper were formed.

1. Introduction

Steam reforming of methanol (SRM) is one of the alternative ways to produce hydrogen (H_2). Due to its high purity product stream, this technique has received much attention as a potential technology to feed hydrogen to the proton exchange membrane fuel cells (PEMFCs) to generate electricity [1]. Normally, SRM is more favorable at high temperatures because it is an endothermic reaction thus there is a requirement for heating the reagents. However, the main drawback of the SRM is the co-existence of a side reaction—methanol decomposition (DM)—which is favored at high temperatures and also forms CO which poisons the Pt electrode in PEMFCs [2–4]. Low temperature (200–400 °C) SRM can be beneficial because of the lower amount of CO formed and energy saved. However, improvement of SRM activity at low-temperatures depends on many parameters, such as H_2O/CH_3OH molar ratio [5,6], the types of catalyst selection [7], reaction temperature [1,2], and gas hourly space velocity [4].

In this study, we focused on developing more active catalysts starting with the support. Ceria (CeO_2) support is attractive for SRM reaction since it has high oxygen vacancies to store the oxygen atoms of the feed reactants, and then release them in an active form to activate the reaction. This characteristic property of the CeO_2 has been widely used in water-gas shift reaction (WGSR) [8] and preferential CO oxidation (PROX) [9]. In addition, oxygen vacancies and redox properties of ceria have been improved by inserting cationic species ($M^{\delta+}$ where M = Fe, Zr, Mn, etc.) into the ceria lattice to form $Ce_xM_{1-x}O_2$ solid solutions, which have also significantly enhanced the catalytic activities in many reactions [2,10,11]. Among the mixed oxides supports, the CeO_2-ZrO_2 support has better thermal stability, smaller crystallite size, and lower coke formation—a major cause of catalyst deactivation [12,13]. Based on this we decided to use CeO_2-ZrO_2 as the support for our SRM catalyst. However, the creation in the efficient oxygen vacancies of the CeO_2-ZrO_2 support depends on the preparation route used [14,15].

For the active metal in the catalyst, we chose gold (Au) because of its well known CO oxidation activity [11,16]. Recent studies carried out in our laboratory with ceria and CeO_2-Fe_2O_3 found that the Au supported over CeO_2 and CeO_2-Fe_2O_3 exhibited the superior activity (100% CH_3OH conversion) in the low-temperature range of 300–400 °C, with modest CO production (10%, v/v) [2,3,5]. The activity of gold catalysts strongly depends on the Au dispersion, Au particle size, the interaction between Au and the support, and the promotion by another active metal [2,17,18]. The combination of Cu and Au as a bimetallic catalyst has shown high catalytic activity in many reactions. The Au–Cu alloy was found to be an active phase [19–21], when compared to the individual Au and Cu catalysts. Likewise, the classification of Au–Cu alloy could be differentiated depending on (i) the origin of the CuO species: highly dispersed and bulky types [22,23] and/or (ii) the oxidation states of the Cu species

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(Cu^{2+}, Cu^{+}, and Cu^{0}) [22]. Liu et al. also reported on the roles of Cu which helped prevent Au sintering and stabilize the Au particle size, as well as the Au dispersion [24].

In this study, a series of Au-Cu/CeO_2-ZrO_2 catalysts prepared by the deposition–precipitation technique (DP) were investigated for SRM in the 200–500 °C range. The parameters considered involved Au/Cu atomic ratio, gas pretreatment, total metal loading, and calcination temperature. The physical–chemical properties of the catalysts were characterized by means of XRF, XRD, H_2-TPR, UV–vis, TPO, and TEM.

2. Experimental

2.1. Catalyst preparation

The CeO_2-ZrO_2 mixed oxide support with Ce/(Ce + Zr) of 0.75 was initially prepared by the co-precipitation (CP) method to achieve a $Ce_{0.75}Zr_{0.25}O_2$ solid solution. Three 0.1 M aqueous solutions of cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$; Aldrich), zirconium (IV) oxide chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$; Merck), and Na_2CO_3 (Riedel-de Haen) were mixed in appropriate amounts under vigorous stirring at 80 °C and pH of 8. Afterward, the precipitate was washed, dried, and calcined in air at 400 °C for 4 h in order to obtain the support.

For the second step, gold was deposited on the $Ce_{0.75}Zr_{0.25}O_2$ support with 3 wt% loading. An aqueous solution of $HAuCl_4 \cdot 3H_2O$ (0.005 M, Alfa AESAR) was heated to 80 °C and adjusted to pH 8 with Na_2CO_3. After the resulting solution was stirred for 1 h, the suspension was washed with warm deionized water to eliminate the residue ions. The deionized precipitate was dried at 110 °C and calcined in air at 400 °C for 4 h. For the Cu/$Ce_{0.75}Zr_{0.25}O_2$ catalyst, the preparation was similar to gold deposition, but the metal solution was used as copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$; MERCK), and the solution was adjusted to pH 7.

For the bimetallic Au-Cu/$Ce_{0.75}Zr_{0.25}O_2$ catalyst preparation, two metal aqueous solutions—$Cu(NO_3)_2 \cdot 3H_2O$ and $HAuCl_4 \cdot 3H_2O$—were used as depositing agents, and then heated to 80 °C with the pH adjusted to 7 by an addition of Na_2CO_3. The appropriate amounts of mixing solutions followed the Au/Cu ratio of 3/1, 1/1, and 1/3. The total loading was varied in the range of 3–7 wt% under the suitable Au/Cu ratio. After the resulting solution was stirred for 1 h, the suspension was washed and dried as same as the deposition step. Finally, the catalyst was calcined in air at various temperatures (200–400 °C) for 4 h.

2.2. Catalyst characterization

An X-ray fluorescence spectrometry, XRF (AXIOS PW4400) was used to determine the actual surface (Au, Cu, Ce, and Zr) composition.

The XRD measurement was carried out on a JEOL X-ray diffractometer system (JDX-3530) with a CuK_{α} (1.5406 Å) X-ray source operating at 40 kV and 30 mA.

The size and distribution of the Au particles deposited on the supports were directly observed by a transmission electron microscope, TEM (JEOL, JEM 2010), at an accelerating voltage of 200 kV in bright field mode. Before being transferred into the TEM chamber, the samples were dispersed in ethanol and then dropped onto a copper grid. The volume-area average Au particle size diameter (d_{TEM}) was calculated from the following formula: $d_{TEM} = \Sigma(n_i d_i{}^3)/(n_i d_i{}^2)$, where n_i is the number of Au particles of diameter d_i.

The UV–vis spectroscopy experiments checked for the presence of different states of oxidation of the contained metals (which were recorded on a Shimadzu UV spectrophotometer 2550). The measurements were performed on air-exposed samples at ambient temperature between 200 and 800 nm. The absorption intensity was expressed using the Kubelka–Munk function, $F(R_\infty) = (1 - R_\infty)^2/(2R_\infty)$, where R_∞ is the diffuse reflectance from a semi-infinite layer.

Temperature-programmed reduction (TPR) was utilized for the evaluation of the reducibility of the catalysts and was used with 10% H_2 in Ar at 30 mL/min as the reducing gas in a conventional TPR reactor equipped with a thermal conductivity detector. The reduction temperature was raised from 30 to 850 °C at a ramp rate of 10 °C/min.

The amount of carbon formation on the spent catalysts was measured by means of temperature-programmed oxidation (TPO). About 50 mg of the powdered samples was packed in a quartz tube reactor before being heated from 100 °C, with a heating rate of 12 °C/min, to 900 °C under a flow of 2% O_2/He, at using a gas flow rate of 30 mL/min.

2.3. Catalytic activity measurements

The SRM reaction was carried out in a fixed-bed reactor containing 100 mg of 80–120 mesh Au-Cu/CeO_2-ZrO_2 catalysts under atmospheric pressure with a reaction temperature of 200–500 °C. A mixture of distilled water and methanol in a syringe was injected continuously by a syringe pump at a rate of 1.5 mL h^{-1} to a vaporizer to produce a vapor of methanol and steam, which was mixed with the He carrier gas before entering the catalytic reactor. The H_2O/CH_3OH molar ratio was fixed at 2/1. For the gas pretreatment, the 3 wt% of the optimum Au/Cu ratio was chosen for further pretreating with H_2 and O_2 gases at 200 °C for 2 h before testing the SRM. The total metal loadings and calcination temperatures were varied from 3 to 7 wt% and 200 to 400 °C, respectively. The stability tests of the Cu/$Ce_{1-x}Zr_xO_2$, Au/CeO_2-Fe_2O_3 [2], and Au-Cu/$Ce_{1-x}Zr_xO_2$ were investigated on stream for 18 h for comparison purposes. The gas hourly space velocity (GHSV) was 21 000 mL/g-cat. h. The product gases (e.g. H_2, CO, CO_2, and CH_4) from the reactor were analyzed both qualitatively and quantitatively by auto-sampling in an on-line gas chromatograph, Agilent 6890N, with a packed carbosphere (80/100 mesh) column (10 ft × 1/8 in.) and a thermal conductivity detector (TCD). The selectivity of each product gas was defined by the mole percentage in the product stream. No methane formation was observed.

3. Results and discussion

3.1. Catalyst characterization

According to the chemical composition of each catalyst, as recorded in Table 1, most catalysts have actual metal compositions close to those of the expected values, including the Ce and Zr compositions. However, the Au3Cu1 sample has the actual Au/Cu ratio of 1.61, which is less than the expected value of 3, indicating a deviation of Au and Cu concentrations during the preparation step. The chemical and physical properties of the bimetallic Au-Cu/$Ce_{0.75}Zr_{0.25}O_2$ catalysts are summarized in Table 2. The lattice constant (a_0) of the ceria in the CeO_2-ZrO_2 mixed oxides was 0.539–0.540 nm, which was smaller than that of pure CeO_2 (0.544). This is attributed to the formation of a stable $Ce_{1-x}Zr_xO_2$ solid solution [14,23], resulting in the shrinkage of the lattice parameter [25,26]. For the XRD patterns of the catalysts with various Au/Cu ratios, as presented in Fig. 1A, no copper species diffractions are observed, implying that if pure copper or copper oxide were formed, their crystallite sizes were very small [23,24]. In comparison to pure Au/$Ce_{0.75}Zr_{0.25}O_2$ (Au/Cu = 1/0), the Au (1 1 1) diffraction peaks started to shift from 38.34° to 38.17° in the