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Effect of support composition and metal loading on Au catalyst activity in steam reforming of methanol

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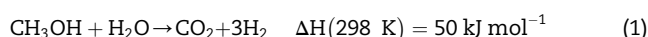
ABSTRACT

Gold (Au) supported on CeO₂–Fe₂O₃ catalysts prepared by the deposition-coprecipitation technique were investigated for steam reforming of methanol (SRM). The 3 wt% Au/CeO₂–Fe₂O₃ sample calcined at 400 °C achieved 100% methanol conversion and 74% hydrogen yield due to a strong Ce–Fe interaction in the active solid solution phase, Ce_xFe_{1–x}O₂. The sintering of Au particles was observed when the highest metal content of 5 wt% was registered, which worsened the SRM activity. According to the TPR and TPO analysis, it was found that the transformation of the α-Fe₂O₃ structure in the mixed oxides and the coke deposition were the main factors for the rapid deactivation of the catalyst.

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1. Introduction

Due to the demand for new energy carriers worldwide, many methods for efficient hydrogen production are still being investigated to find the best candidate [1–3]. Methanol (CH₃OH) is widely acknowledged as a good reactant for the high-purity of hydrogen due to its low boiling point and high H/C ratio, which reduces the soot and coke formation [4–7]. Normally, hydrogen production based on a methanol source can be classified into three main reactions: methanol decomposition (DM), steam reforming of methanol (SRM), and partial oxidation of methanol (POM). SRM is also an endothermic reaction which obtains the highest H₂ yield (3 mol H₂/1 mol CH₃OH) with lower amounts of CO and low temperature operation (200–400 °C), as shown in Eq (1).



However, the activity of SRM reaction depends on the type of catalyst used. Accordingly, it is necessary to produce high H₂ purity which follows the requirement in PEM fuel cells (CO < 10 ppm) [8–10].

Many previous investigations mainly focused on Cu-based catalysts due to their high activity for SRM reaction. Unfortunately, the pyrophoric characteristic seems to be a crucial issue, which causes the rapid deactivation and sintering of these catalysts when the catalyst is carried out at high temperatures (>270 °C) [11–13]. To avoid this problem, there has been significant activity to develop a new catalyst for this in recent years. Only a few studies related to hydrogen production from methanol over Au-based catalysts are

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reported; however, this catalyst is well known as an active catalyst in many reactions including preferential CO oxidation (PROX) [14] and water-gas shifted reaction (WGS) [15]. Yi et al. found that the Au/CeO₂ catalyst could obtain full methanol conversion at 300 °C over the SRM reaction with no deactivation [11].

The activity of gold catalysts strongly depends on the Au dispersion, Au natural site, Au particle size, and interaction between Au and support (or by itself) [16]. Our previous work found an improvement in Au–Au interaction of 5 wt% Au/CeO₂ catalysts, which facilitated extreme catalytic activity in the oxidative methanol reforming (OSRM) [17]. Ceria (CeO₂) is defined as an interesting support because it has high oxygen storage capacity (OSC) or oxygen vacancy, which allows itself to store and release active oxygen to provide good performance in SRM reaction [18,19]. In further studies, the chemical properties of ceria were successively developed by the incorporation of triple cations, M³⁺ (M = Fe, La, etc), into the ceria lattice [20–22]. This incorporation can enhance the formation of vacancies in the anion sublattice during the charge balancing, where the redox properties in ceria can be improved. The addition of another interesting support, Fe₂O₃, with CeO₂ has been receiving much attention due to the creation of an active solid solution phase (Ce_xFe_{1-x}O₂), which could be beneficial for many applications [20,23,24]. The Au/CeO₂–Fe₂O₃ showed high activity for the PROX and WGS when the strong Ce–Fe interaction was formed in solid solution [25,26]. Based on previous studies, there are a number of possibilities for catalyst modification by creating oxygen vacancies on the support [27].

In this study, a series of Au/CeO₂–Fe₂O₃ catalysts prepared by the deposition–precipitation technique (DP) were investigated for SRM in the temperature range of 200–400 °C.

2. Experimental

2.1. Catalyst preparation

Various ratios of mixed oxides (CeO₂–Fe₂O₃) supports—Ce:Fe = 8:1, 1:1, and 1:8—were prepared by a co-precipitation method, while the pure CeO₂ and Fe₂O₃ supports were prepared by a precipitation method. The Au/CeO₂, Au/Fe₂O₃, and Au/CeO₂–Fe₂O₃ catalysts were prepared by the deposition–precipitation technique. For support preparation, cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O) (Aldrich), iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O) (Aldrich), and Na₂CO₃ (Riedel-de Haen) were mixed under vigorous stirring condition at 80 °C and pH 8. Afterward, the precipitate was washed, dried, and calcined in air at 400 °C for 4 h in order to obtain the CeO₂–Fe₂O₃ supports.

Gold was loaded on the supports (CeO₂, Fe₂O₃, and CeO₂–Fe₂O₃). An aqueous solution of HAuCl₄·3H₂O (Alfa AESAR) was heated at 80 °C and adjusted to pH 8 with Na₂CO₃. 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 various temperatures (200–400 °C) for 4 h. The CeO₂–Fe₂O₃ support at each composition (Ce:Fe atomic

ratio) was designated as CeXFeY, where X and Y are the atomic ratio of Ce and Fe, respectively.

2.2. Catalyst characterization

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 (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 were then dropped onto a copper grid. The volume–area average Au particle size diameter (d_{TEM}) was calculated from the following formula: $d_{\text{TEM}} = \sum n_i d_i^3 / \sum n_i d_i^2$, where n_i is the number of Au particles of diameter d_i .

DR/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 between 200 and 800 nm at ambient temperature. 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. An X-Ray Fluorescence Spectrometry, XRF (AXIOS PW4400) was used to determine the actual surface (Au, Ce, and Fe) composition.

Temperature-programmed reduction (TPR) was utilized for the evaluation of the reducibility of the catalysts and was employed by using 10% H₂ in Ar at 30 mL/min as a 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 of the spent catalysts was measured by means of temperature-programmed oxidation (TPO). Approximately 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% O₂/He 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 with 80 to 120 mesh holes containing 100 mg of the Au/CeO₂–Fe₂O₃ catalysts under atmospheric pressure with a reaction temperature of 200–400 °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 H₂O/CH₃OH molar ratio was fixed constantly at 2/1. The Au contents and calcination temperatures were varied from 1 to 5 wt% and 200 to 400 °C, respectively. Finally, the stability of the prepared catalysts was tested for 10 h. The gas hourly space velocity (GHSV) was kept at 21,000 mL/g-cat. h. The product gases (e.g. H₂, CO, CO₂, and CH₄) 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 inch) and

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