Journal of Industrial and Engineering Chemistry 20 (2014) 961–971

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Effect of steam content and O_2 pretreatment on the catalytic activities of $Au/CeO_2–Fe_2O_3$ catalysts for steam reforming of methanol

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ARTICLE INFO

Article history:
Received 24 January 2013
Accepted 20 June 2013
Available online 28 June 2013

Keywords:
Steam reforming
Methanol
Hydrogen
Carbonate
Au catalyst

ABSTRACT

The $Au/CeO_2–Fe_2O_3$ prepared by deposition–precipitation were studied by steam reforming of methanol at a reaction temperature range of 200–400 °C. Complete methanol conversion was obtained at the optimal steam/methanol ratio of 2 at 400 °C. A high steam content strongly depressed both methanol conversion and hydrogen concentration since this led to a complex mechanism and the formation of carbonate and formate species. After pretreating with oxygen, the catalytic activity dramatically decreased with the presence of an inhomogeneous $Ce_xFe_{1-x}O_2$ solid solution phase; the covering Au sites by the free α-Fe_2O_3 particles; and an agglomeration of both free α-Fe_2O_3 and Au particles.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs)—a green technology—can generate electricity without emissions by reactions between H_2 and O_2 in the feed [1]. However, the requirement of high H_2 purity feed linking with the performance of the Pt electrode in PEMFC does not allow the amount of CO contamination in the feedstream from H_2 production process to be higher than 10 ppm. To achieve high purity of this energy carrier (H_2), the steam reforming process of liquid hydrocarbon and alcohol fuels was used to provide a suitable feed for PEMFC. Methanol (CH_3OH) has received much attention by virtue of fact that the operating temperature can be as low as 200–400 °C, when compared with other oxygenated compounds and hydrocarbon fuels [2,3]. Normally, the steam reforming of methanol (SRM) is an endothermic reaction that requires external heat from the surroundings to be favorable at a high temperature. However, CO can be produced as a by-product via methanol decomposition (DCM), which depresses the H_2 purity during the SRM [4,5]. In order to improve SRM activity in the low-temperature range, many effective parameters: H_2O/CH_3OH ratio [5], types of catalyst selection [6], catalyst preparation method [7], and reaction temperature [4] are considered.

Among the catalysts studied for H_2 production and CO reduction, one of the most active catalysts is a copper-(Cu-) based catalyst, which exhibits superior catalytic activity; however, the thermal stability is less at $T > 270$ °C because of its pyrophoric characteristic [8]. Recently, the selection of noble metal catalysts has been developed to be more active, especially for the gold-(Au-) based catalysts which play a role in reducing CO under a low temperature operation via CO oxidation [9] and water-gas shift (WGS) reactions [10]. It has also been found that the high H_2 purity could be achieved by the introduction of Au metal in methanol reforming, and its activity strongly depends on the gold particle size [4,5], method of preparation [11], and type of support [12]. For the metal oxide support selection, ceria (CeO_2) has an oxygen storage capacity, which can store and release active oxygen to achieve good catalytic activity. Besides, the addition of hematite (Fe_2O_3) in the ceria is known to form the solid solution phase ($Ce_xFe_{1-x}O_2$), resulting in an increase in both the oxygen vacancies or storage sites of the support, and its reducibility [13,14]. In 2012, Au supported on CeO_2 and $CeO_2–Fe_2O_3$ mixed oxides supports exhibited excellent performance in H_2 yield for both oxidative steam reforming of methanol (OSRM) and SRM, while the CO amount was produced in minute amounts [4,5,15]. We have previously reported that our catalyst with a Ce:Fe atomic ratio of 1:1 calcined at 400 °C exhibited good activity for SRM because these conditions provided a homogeneous solid solution

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http://dx.doi.org/10.1016/j.jiec.2013.06.029

(strong Ce–Fe interaction) and strong Au–support (Au–Fe^{3+}) interaction [4]. Interestingly, it is well known that the catalytic performance of Au catalysts also depends on the pretreatment conditions and in the presence of O_2, where the Au catalysts exhibit stronger catalytic activity in CO oxidation [16]. The O_2 pretreatment may affect the change of the solid solution phase and interaction of the prepared catalyst, and it might be beneficial for the regeneration step in minimizing coke formation via coke gasification on the spent catalyst surface [17]. Hence, the investigation on applying gas pretreatment with the physical-chemical changes of the Au/CeO_2–Fe_2O_3 catalyst must be necessary.

Not only the catalyst preparation route, but the difference in feed composition also affected the catalytic activity of the catalyst during the SRM reaction. For instance, some authors reported that the carbonate and formate species could block the active sites or Au-metal oxide interface [18,19] and then lower the catalytic performance when the steam content was increased in the feedstream. Similarly, these species were defined as the poisoning substances that deposited and blocked the active sites on the surfaces of Au/CeO_2, Au/CeO_2–Fe_2O_3, and Au–CuO/CeO_2 catalysts when varying the steam content in OSRM [5,15,20]. In contrast, the positive effect of water or steam addition was proven by Schubert et al. [21] and Costello et al. [22], and the mechanism pathways of formate/or carbonate species linking with the steam addition had been elucidated only on the WGS reaction. On the other hand, another explanation based on the reaction pathways of thermodynamic evaluation had been proposed to clarify the effect of feed concentration instead [1]. In order to better understand, a study on the surface change of the Au catalyst during the steam variation in the SRM feed was needed.

In the present work, we investigated the effects of the H_2O/CH_3OH molar ratio and O_2 pretreatment on the catalytic activity of Au/CeO_2–Fe_2O_3 catalysts for SRM. Many characterization techniques—XRF, XRD, TPR, FTIR, FT-Raman, TEM, and TPO—were undertaken to clarify the catalytic properties of the Au catalysts.

2. Experimental

2.1. Catalyst preparation

For CeO_2–Fe_2O_3 support preparation, cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) (Aldrich), iron (III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) (Aldrich), and Na_2CO_3 (Riedel-de Haen) were mixed with vigorous stirring at 80 °C and pH 8 via the co-precipitation technique. Finally, the precipitate was washed, dried, and calcined in air at 400 °C for 4 h to obtain the CeO_2–Fe_2O_3 supports.

For the 3 wt% Au deposition, similar techniques previously described were used [23,24]. The CeO_2–Fe_2O_3 support (Ce:Fe atomic ratio of 1:1) was suspended in an aqueous solution of $HAuCl_4.3H_2O$ (0.005 M), which was purchased from Alfa AESAR. The suspension was heated at 80 °C and adjusted to the required pH (pH 8) with vigorous stirring using Na_2CO_3. After the resulting solution was stirred for 1 h and cooled to room temperature, the suspension was washed with warm deionized water to eliminate residue ions. The deionized precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 h.

2.2. Catalyst characterization

The crystal structures of the fresh and spent catalysts were characterized by X-ray diffraction (XRD, JDX-3530) equipped with a CuK_α (1.5406 Å) X-ray source. A generator was operated at 40 kV and 30 mA. Samples were run in a continuous scan mode in the range of 20–90°.

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 in the TEM chamber, the samples were dispersed in ethanol and were then dropped onto a copper grid.

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

The Fourier transform infrared spectra (FTIR) of the samples were recorded using a Thermo Nicolet Nexus 670 FTIR spectrometer in absorbance mode at 32 scans with a resolution of 4 cm^{-1}. The spectra in the frequency range of 4000–400 cm^{-1} were obtained by using a deuterated triglycerinesulfate detector (DTGS) with a specific detectivity of 1×10^9 cm $Hz^{1/2}$ w^{-1}.

The Fourier transform Raman spectra (FT-Raman) of the samples were recorded using a Perkin Elmer (Spectrum GX) FT-Raman spectrometer using a Nd-YAG laser (1064 nm) in absorbance mode at 2000 scans with a resolution of 16 cm^{-1}. The frequency range of 3500–200 cm^{-1} was obtained.

Temperature-programmed reduction (TPR) was employed by using 10% H_2 in Ar at 30 mL min^{-1} 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^{-1}.

For the temperature-programmed oxidation (TPO) experiment, approximately 50 mg of the powdered samples was packed in a quartz reactor and a thermocouple was placed at the top of the catalyst layer. The sample was heated from 100 °C with a heating rate of 12 °C min^{-1} to 900 °C under a flow of 2% O_2/He using a gas flow rate 30 mL min^{-1}.

2.3. Catalytic activity measurements

Catalytic activity measurements were carried out in a fixed-bed reactor containing 100 mg of Au/CeO_2–Fe_2O_3 catalyst. A mixture of 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 (or S/M) molar ratio was varied proportionally from 1/1 to 4/1. The SRM reaction was conducted at a reaction temperature of 200–400 °C under atmospheric pressure.

The stability of the prepared catalysts was tested for 10 h. For the O_2 pretreatment, the fresh catalyst was pretreated at a O_2 flow rate of 30 mL min^{-1} at 200 °C for 2 h. The gas hourly space velocity (GHSV) was kept at 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 (GC), Agilent 6890N, equipped 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 during this study.

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows the chemical and physical properties of the series of Au/CeO_2–Fe_2O_3 catalysts. The actual compositions of all prepared catalysts (Au, Ce, and Fe) were almost the same and close to the expected values. In comparison to the lattice constant of the pure CeO_2 support (a_0 = 0.544 nm) with the Au deposition, changes in the lattice constant indicated a solid solution was formed. Generally, for $a_0 < 0.544$, it agrees well with the existence of a solid solution form, where the Fe^{3+} (r = 0.064 nm) has already