Hydrogen production by partial oxidation of methanol over bimetallic Au–Ru/Fe$_2$O$_3$ catalysts

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Abstract

Hydrogen production by partial oxidation of methanol (POM) was investigated over Au–Ru/Fe$_2$O$_3$ catalyst, prepared by deposition–precipitation. The activity of Au–Ru/Fe$_2$O$_3$ catalyst was compared with bulk Fe$_2$O$_3$, Au/Fe$_2$O$_3$ and Ru/Fe$_2$O$_3$ catalysts. The reaction parameters, such as O$_2$/CH$_3$OH molar ratio, calcination temperature and reaction temperature were optimized. The catalysts were characterized by ICP, XRD, TEM and TPR analyses. The catalytic activity towards hydrogen formation is found to be higher over the bimetallic Au–Ru/Fe$_2$O$_3$ catalyst compared to the monometallic Au/Fe$_2$O$_3$ and Ru/Fe$_2$O$_3$ catalysts. Bulk Fe$_2$O$_3$ showed negligible activity towards hydrogen formation. The enhanced activity and stability of the bimetallic Au–Ru/Fe$_2$O$_3$ catalyst has been explained in terms of strong metal–metal and metal–support interactions. The catalytic activity was found to depend on the partial pressure of oxygen, which also plays an important role in determining the product distribution. The catalytic behavior at various calcination temperatures suggests that chemical state of the support and particle size of Au and Ru plays an important role. The optimum calcination temperature for hydrogen selectivity is 673 K. The catalytic performance at various reaction temperatures, between 433 and 553 K shows that complete consumption of oxygen is observed at 493 K. Methanol conversion increases with rise in temperature and attains 100% at 523 K; hydrogen selectivity also increases with rise in temperature and reaches 92% at 553 K. The overall reactions involved are suggested as consecutive methanol combustion, partial oxidation, steam reforming and decomposition. CO produced by methanol decomposition is subsequently transformed into CO$_2$ by the water gas shift and CO oxidation reactions.
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1. Introduction

Fuel cell system offers high potential for efficiency and reduces emission of pollutants in power generation [1,2]. The most promising fuel cells would seem to be the ones equipped with proton exchange membrane (PEM) using hydrogen [3,4]. However, the distribution and on-board storage of hydrogen are major hurdles. In order to avoid storing high-pressure hydrogen, the fuel can be generated in an on-board fuel processor. Methanol is a preferred source of on-site hydrogen production because of its high ratio of hydrogen to carbon and abundant storage [5]. There are several routes for hydrogen production from methanol, such as methanol decomposition (MD) [5,6], steam reforming (SRM) [7,8], oxidative steam reforming (OSRM) [9,10] and partial oxidation (POM) [11–15]. Until the mid-1980s, it was

believed that steam reforming of methanol was the only successful process for the production of hydrogen from methanol. Partial oxidation of methanol in the absence of steam offers several advantages over steam reforming, as the reaction is exothermic, uses air or oxygen as oxidant instead of steam and so steam generation unit is not required. In addition to that, the reaction rate of POM is higher than SRM over copper catalysts [16]. Therefore, partial oxidation of methanol (POM) has been suggested as a suitable route for hydrogen extraction from methanol.

Previous studies on POM to produce hydrogen showed that, supported copper and palladium catalysts are found to be active [11–13]. Recently, we have produced a fruitful result on the production of hydrogen by POM using supported gold catalysts [15,17]. Further development of new efficient catalyst systems that exhibit an improved long-term stability and selectivity towards hydrogen production are highly desired. In recent years, bimetallic catalysts have received a great deal of attention because many studies have shown that the presence of

the second component may induce significant changes in both activity and stability for catalytic reactions [18,19]. Various bimetallic combinations containing gold have been used successfully for different reactions such as, selective oxidation of glycerol, steam reforming of hydrocarbon, ethylene oxidation and water gas shift reactions [20–23]. In the present study, catalytic activity of Au–Ru/Fe$_2$O$_3$ catalyst was tested for partial oxidation of methanol (POM) to produce hydrogen. The reason for choosing Au–Ru/Fe$_2$O$_3$ catalyst is, supported ruthenium catalyst is reported to be active for partial oxidation of ethanol to produce hydrogen [24] and preferential oxidation of CO in excess of H$_2$ [25]. Since supported gold catalysts are active for POM to produce hydrogen, a combination of gold and ruthenium metals was used in the present study.

The objective of the present investigation is to compare the catalytic activity of bulk Fe$_2$O$_3$, Au/Fe$_2$O$_3$, Ru/Fe$_2$O$_3$ and Au–Ru/Fe$_2$O$_3$ catalysts prepared by deposition–precipitation technique for the formation of hydrogen by partial oxidation of methanol (POM). In order to develop an efficient catalytic system, attention has been paid to the optimization of reaction parameters such as O$_2$/CH$_3$OH molar ratio, calcination temperature and reaction temperature on the performance of Au–Ru/Fe$_2$O$_3$ catalysts for hydrogen formation by POM. To learn about the interrelationship between the characteristics of the catalyst and catalyst performance in POM, the catalyst characterization included is inductively coupled plasma mass spectrometer (ICP-MS), X-ray diffraction (XRD), transmission electron microscopy (TEM) and temperature-programmed reduction (TPR) analyses.

2. Experimental

2.1. Catalyst preparation

The Au–Ru/Fe$_2$O$_3$ catalyst with 1 wt.% Au and 1 wt.% Ru was prepared by a deposition–precipitation method [23], using HAuCl$_4$·3H$_2$O (Fluka), RuCl$_3$·3H$_2$O (Johnson Matthey PLC) and Fe(NO$_3$)$_3$·9H$_2$O (Fluka) as starting materials. Dilute NH$_4$OH was used as precipitant. For comparative study 2 wt.% Au/Fe$_2$O$_3$ and 2 wt.% Ru/Fe$_2$O$_3$ catalysts were prepared using deposition–precipitation method. In the preparation procedure, the required amount of Fe(NO$_3$)$_3$·9H$_2$O (Fluka) was dissolved in 500 ml distilled water and precipitated using dilute aqueous ammonium hydroxide solution at ambient temperature until the pH reached a value of 8.6. To this preformed gel, requisite quantity of HAuCl$_4$·3H$_2$O and/or RuCl$_3$·3H$_2$O were added under vigorous stirring at 348 K. The slurry was then aged for 6 h. The resultant precipitates were filtered and washed carefully until all chloride ions were removed. The sample was dried at 373 K for 12 h and calcined in air at different temperatures for 4 h. Metal content analysis by ICP method shows that in all the catalyst samples gold and ruthenium loading is close to the target loading. With an initial loading of 2 wt.% Au in Au/Fe$_2$O$_3$ catalyst and 2 wt.% Ru in Ru/Fe$_2$O$_3$ catalyst, resulted in a loading of 1.9 wt.% Au and 1.8 wt.% Ru, respectively. In Au–Ru/Fe$_2$O$_3$ catalysts, with an initial loading of 1 wt.% Au and 1 wt.% Ru, resulted in a loading of 0.95 wt.% Au and 0.88 wt.% Ru, respectively.

The pure α-ferric oxide was also prepared for comparative studies by the hydrolysis of ferric nitrate using dilute aqueous ammonium hydroxide solution at ambient temperature until the pH reached a value of 8.6. The sample was filtered, washed, dried at 373 K for 12 h and then calcined in air at 673 K for 4 h.

2.2. Characterization

The gold and ruthenium content of the catalyst precursor were determined with an inductively coupled plasma mass spectrometer (Kortron plasmakon, Model S-35). For this, the catalyst samples were dissolved in aqua regia and diluted with demineralized water to concentrations within the detection range of the instrument before performing the analysis.

X-ray powder diffraction (XRD) patterns of samples of the catalyst precursors as well as the supports were obtained in an X-ray diffractometer (Schimadzu, Model XD-5) using Cu Kα radiation with a wavelength of 1.5406 Å, from 20 to 70° at a rate of 0.04°/s.

Transmission electron microscopy (TEM) studies were performed on a JEOL JEM-2000FX II instrument operated at 160 kV. To obtain suitable samples for TEM characterization, the powders were dispersed in ethanol by ultrasonication. The samples were mounted on a micro-grid carbon polymer supported on a copper grid by placing a few droplets of a suspension followed by drying at 333 K.

Temperature-programmed reduction (TPR) of the catalyst was performed in a U-shaped micro-reactor made of quartz, surrounded with a furnace controlled by a programmed heating system. Prior to the TPR experiment, 40 mg of the catalyst sample was pretreated under flowing Ar (20 ml/min) at room temperature for 1 h. After the pretreatment, a reducing gas composed of 5% H$_2$ plus 95% Ar was employed at a flow rate of 20 ml/min, with a heating ramp of 10 K/min from 323 to 973 K. The amount of the consumed H$_2$ was determined by a thermal conductivity detector (TCD).

2.3. Activity measurements

Partial oxidation of methanol (POM) was carried out using an apparatus, which has been described in detail elsewhere [15]. The reaction was carried out at atmospheric pressure and at 523 K, using a U-shaped micro-reactor made of quartz (i.d. = 4 mm). The reactor was located in a programmable furnace with a type K thermocouple placed in the center of the catalyst bed. Typically, 40 mg of catalyst was used in each experiment. Methanol was fed into the pre-heater by means of a Cole-Parmer liquid pump (Model: 77120–30) at a rate of 0.013 ml/min. The oxygen and argon (diluent) flows were adjusted by Brooks 5850E mass flow controllers. The total flow was 60 ml/min. Except especially mentioned the O$_2$/CH$_3$OH molar ratio was kept at 0.5. The reaction products were analyzed on-line using two gas chromatographs (GC) equipped with thermal conductivity detector and porapak Q and carbosieve S-II columns.

In the following discussion, methanol conversion, hydrogen selectivity, carbon monoxide and methane selectivity are