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# Microwave irradiation assisted rapid synthesis of Fe–Ru bimetallic nanoparticles and their catalytic properties in water-gas shift reaction

Jian-Quan Du<sup>a</sup>, Yong Zhang<sup>b</sup>, Tian Tian<sup>b</sup>, Shan-Cheng Yan<sup>b</sup>, Hai-Tao Wang<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry, Taishan University, Taian, 271021, PR China

<sup>b</sup> State Key Laboratory of Bioelectronics, School of Biological Science and Medical Engineering, Southeast University, Nanjing, 210096, PR China

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## 1. Introduction

The design and controlled fabrication of nanoscaled materials with functional properties have attracted much interest due to their various applications such as catalysts, magnetic devices, single electron transistors, and optoelectronics [1–4]. Recently, core-shell and alloy bimetallic nanoparticles have been extensively studied because they can exhibit unique electronic, optical, and catalytic properties that are absent in corresponding monometallic nanoparticles [5–8]. Furthermore, the addition of second metal provides a method to control the chemical and physical properties of nanoparticles.

The polyol method was used for the preparation of nanoparticles [9–14] in the past decade. In this method, a polyol (for example, ethylene glycol (EG)) was used as both a reducing reagent and a solvent. The glycol method using conventional heating requires a relatively long preparation time (usually several hours or longer). Compared with the conventional heating, microwave heating is promising due to its unique effects, such as rapid volumetric heating, higher reaction rates and shorter reaction time, higher reaction selectivity and energy saving and leads to the formation of uniform nanoparticles.

The water-gas shift reaction (WGSR) is an industrially important process that can be employed in the Fischer–Tropsch reaction and in

## ABSTRACT

Fe–Ru bimetallic nanoparticles were prepared by a microwave irradiation assisted glycol reduction method using poly-N-vinyl-2-pyrrolidone (PVP) as protective agent. The structure and morphology of the nanoparticles were characterized by X-ray diffraction (XRD), energy-dispersive X-ray analysis (EDXA) and high-resolution transmission electron microscopy (HRTEM). EDXA and XRD analysis confirmed the presence of Fe and Ru. The bimetallic nanoparticles were subsequently loaded onto an MgAl<sub>2</sub>O<sub>4</sub> supporter with K<sub>2</sub>O as promoters and used as catalyst for water-gas shift reaction. The results indicated that the FeRu bimetallic nanoparticles exhibit high catalytic activity for water-gas shift reaction due to the synergistic effect between iron and ruthenium. Potassium oxide can enhance the CO selectivity of the catalyst significantly besides increasing the catalyst activity.

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the reduction the CO levels in the ammonia synthesis. WGSR has aroused renewed interest with the respect of supplying highly pure hydrogen as a combustible to fuel cell power generation [15]. Ruthenium deposited on alkali promoted supporters makes catalysts for WGSR very active that they have been accepted as alternatives to the commercially used iron catalysts [16–19].

In this paper, we report a simple method to prepare Fe–Ru bimetallic nanoparticles using 1,2-propanediol to reduce the mixture of FeCl<sub>3</sub> and RuCl<sub>3</sub> with the presence of poly-N-vinyl-2-pyrrolidone (PVP) as protective agent. Additionally, the catalytic properties of the Fe–Ru bimetallic nanoparticles supported on MgAl<sub>2</sub>O<sub>4</sub> for the water-gas shift reaction were investigated.

#### 2. Experimental

#### 2.1. Prepare FeRu bimetallic nanoparticles

The Fe–Ru nanoparticles stabilized by poly-N-vinyl-2-pyrrolidone were prepared by a modified polyol method reported by Feldmann and Metzmacher [12]. In brief, PVP (0.8325 g, 7.5  $\times$  10<sup>-3</sup> mol), RuCl<sub>3</sub>·nH<sub>2</sub>O (0.0371 g, 1.5  $\times$  10<sup>-4</sup> mol) and FeCl<sub>3</sub>·6H<sub>2</sub>O 6H<sub>2</sub>O (0.06 g, 1.5  $\times$  10<sup>-4</sup> mol) were dissolved in 45 mL 1,2-propanediol under stirring to form a dark red solution, then 5 mL 1,2-propanediol solution of ammonia (0.1 M) was added dropwise under vigorous stirring. The mixture was then transferred to a homemade Microwave Oven. A transparent dark brown homogenous colloidal solution of Fe–Ru bimetallic nanoparticles was obtained without any precipitate after microwave heating at an

<sup>\*</sup> Corresponding author. Tel.: +86 25 83790820; fax: +86 25 83790310. *E-mail address*: htwang315@yahoo.com.cn (H.-T. Wang).

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output of 300 W for 3 min. As prepared polyol dispersions of Fe–Ru bimetallic nanoparticles were precipitated using excess acetone. The precipitates were washed with anhydrous acetone in order to remove chloride ions and dried under vacuum and re-dispersed into ethanol–water mixture prior to characterization or use. A series of bimetallic nanoparticles were prepared by vary the molar ration of iron to ruthenium and that of PVP to metal ions.

#### 2.2. Prepare supported catalysts

The bimetallic colloidal solution diluted with deionized water was mixed with a certain amount of MgAl<sub>2</sub>O<sub>4</sub> spinel and the mixture was stirred for 1 h at room temperature. The colloidal particles adsorb instantly onto the MgAl<sub>2</sub>O<sub>4</sub> spinel. Potassium acetate was added as promoter. The solvent was removed with a rotary evaporator, and then the sample was dried at 120 °C overnight and then calcined at 350 °C in Ar for 1.5 h in order to remove organic materials (PVP). The catalyst is labeled as FeRu/ MA. Catalysts Fe/MA and Ru/MA were also prepared by using the same method. Catalyst FeRu/MA(im) was prepared by co-impregnation of MgAl<sub>2</sub>O<sub>4</sub> with a mixture of FeCl<sub>3</sub> and RuCl<sub>3</sub> solutions.

#### 2.3. Characterization

Transmission electron microscopy (TEM) studies were conducted on a Tecnai G2 S-TWIN transmission electron microscope equipped with an energy-dispersive X-ray analysis (EDXA) operating at 200 kV. X-ray diffraction (XRD) patterns were obtained with a Rigaku D/MAX-3B X-ray diffractometer at 35 mA, 30 kV, employing Cu K<sub> $\alpha$ 1</sub> radiation at a scan rate of 3°/ min. The surface morphology of the samples was analyzed with a Hitachi S-570 scanning electron microscope (SEM).

#### 2.4. Catalytic reactions

The WGS reaction was carried out in a continuous flow fixedbed microreactor filled with 0.5 g catalyst and operated at a constant pressure of 0.1 MPa. Steam was introduced by flowing the gas mixture, comprising about 25% CO, 25% H<sub>2</sub>, and 50 vol% N<sub>2</sub>, through double distilled water. The molar ratio of steam to gas (S/ G) was controlled by changing the temperature of water. In current experiments, the steam to gas ratio (S/G) was maintained at 1.0 and space velocity (SV) was 2000 h<sup>-1</sup>. The catalyst was reduced by the gas mixture at 100 °C for 2 h before the reaction. The gas composition was analyzed with two on-line gas chromatographs (GC-122) equipped with TCD and FID, respectively. The activity of the catalyst was evaluated by the carbon dioxide formation.

#### 3. Results and discussion

Due to the size effects, it is important to prepare bimetallic nanoparticles with precise size control. The formation of bimetallic nanoparticles was first confirmed by TEM. The typical TEM images of three colloidal FeRu samples thus formed with their corresponding particle size distribution are shown in parts (a-c) in Fig. 1. The molar ratio of iron to ruthenium is 1:1 in all three samples. The TEM image indicated that all the bimetallic nanoparticles are spherical in shape with uniform and narrow size distribution. When the molar ratio of PVP to metal ions is 5:1, it is found that the nanoparticles mainly consist of particles with a diameter of  $\sim$ 8 nm and some large particles with a diameter of  $\sim$ 10 nm are also observed, as shown in Fig. 1a. When the molar ratio is increased to 10:1, it is clearly seen that most of the nanoparticles are  $\sim$ 5 nm in diameter, as shown if Fig. 1b. When the molar ratio is increased to 50:1, the nanoparticles further become smaller ( $\sim$ 1.4 nm), as shown in Fig. 1c. Obviously, the average size of such colloidal FeRu bimetallic nanoparticles can be controlled by varying the molar ratio of PVP to metal ions.

High-resolution transmission electron microscopy (HRTEM) and EDAX were used to analyze the structure and composition of FeRu bimetallic nanoparticles. Fig. 2 shows the typical HRTEM images of three bimetallic nanoparticles with different molar ratio of iron to ruthenium. The molar ratio of PVP to metal ions is 10:1 in all samples. Judging from the lattice fringes, the bimetallic



Fig. 1. Typical TEM images of FeRu (1:1) bimetallic nanoparticles with PVP/[Fe + Ru] molar ratio 5:1 (a), 10:1 (b), 50:1 (c). Below (a-c) are their corresponding particle size distribution.



Fig. 2. Typical high-resolution TEM images of FeRu nanoparticles with Fe/Ru molar ratio 0.5:1 (a) 1:1 (a) and 1.5:1 (c). The molar ratio of PVP to metal ions for all is 10:1. The scale bar is 5 nm.

nanoparticles appeared to be single crystals. EDAX results indicate that Fe/Ru (0.5:1), Fe/Ru (1:1) and Fe/Ru (1.5:1) nanoparticles have the composition of iron and ruthenium in the molar ratio of 0.43, 0.97 and 1.29, respectively, close to the initial molar ratio in the preparation process. It is difficult to obtain homogenous bimetallic nanoparticles when the Fe/Ru molar ratio is too high.

The formation of bimetallic nanoparticles is possibly due to a strong protective ability of PVP on both Fe and Ru monometallic clusters. In the preparation of bimetallic catalysts, both iron and ruthenium ions could be attached to the C—O group or N atom of PVP. The glycol reduction of these ions then resulted in the formation of bimetallic nanoparticles, which were stabilized by PVP. We have also tried to use PVA and PEG as protective agents to prepare bimetallic nanoparticles. Agglomerated nanoparticles and submicro-particles other than monodipersed nanoparticles were obtained through this microwave irradiation method.

Due to its thermal and steam stability, less acidic surface and attrition resistance, MgAl<sub>2</sub>O<sub>4</sub> spinel was selected as the carrier of supported catalyst for WGS reaction. The MgAl<sub>2</sub>O<sub>4</sub> spinel was prepared according to literature [20]. The formation of MgAl<sub>2</sub>O<sub>4</sub> spinel was confirmed by X-ray diffraction. The X-ray diffraction patterns of fresh and spent Ru/MgAl<sub>2</sub>O<sub>4</sub>, Fe/MgAl<sub>2</sub>O<sub>4</sub> and Fe–Ru/MgAl<sub>2</sub>O<sub>4</sub> catalysts are shown in Fig. 3. X-ray diffraction analysis revealed the presence of MgAl<sub>2</sub>O<sub>4</sub> phase in all fresh and spent samples and the presence of K<sub>2</sub>O phase at the content 8 wt%. In the range of active species loading from 0.6 to 1.2 wt%, there is no other diffraction peaks except that of MgAl<sub>2</sub>O<sub>4</sub> and K<sub>2</sub>O. It can be observed from SEM micrograph of the samples that the supporter is formed by agglomerates of 30–80 nm MgAl<sub>2</sub>O<sub>4</sub> spinel grains. The size of bimetallic nanoparticles was so small that cannot be detected by SEM. Small irregular holes having no characteristic size or shape

among agglomerates were also detected. There is no obvious morphological difference between the fresh and spent samples.

The catalytic activity of the bimetallic catalysts prepared by the colloid method for water-gas shift reaction as a function of FeRu content is plotted in Fig. 4. The FeRu bimetallic nanoparticles with FeRu molar ratio 1:1 and average diameter 5 nm were used in all samples. The changed trend of catalyst activity at 300 °C was similar to that at 265 °C, carbon mono-oxide conversion was first increased with increasing the amount of bimetallic nanoparticles loading up to 1.0 wt% and then decreased with the further increase. The decrease of catalysts activity at high active species content may be caused by the agglomeration of bimetallic nanoparticles. So an optimum bimetallic nanoparticles loading for preparation of the supported catalysts with high catalytic activity is 1.0 wt%.

It is well known that potassium was used as electronical promoters in iron-based water-gas shift catalysts. Potassium can enhance the CO<sub>2</sub> selectivity as well as catalytic activity of supported catalysts in this study significantly. It is well known that ruthenium belongs to platinum-group metals exhibiting strong hydrogenating property [21]. In the case of WGSR, the mixture of substrates and products creates the atmosphere favorable for hydrogenation reaction whose main product is methane [22-24], an undesirable product. According to literature data, ruthenium supported on oxides with acidic character gives catalysts of high activity in CO hydrogenation to hydrocarbons [22–25], while that supported on basic oxides show lower activity in CO hydrogenation [26-28]. Adding potassium as promoter can enhance the surface basicity of MgAl<sub>2</sub>O<sub>4</sub> spinel and affect the reaction direction. The influence of potassium loading on catalytic activity and CO<sub>2</sub> selectivity of supported catalysts at temperature 265 °C was shown in Fig. 5. It was obvious that potassium loading



Fig. 3. X-ray diffraction patterns of catalysts Ru/MA (1), FeRu/MA (2), Fe/MA (3) and FeRu/MA(im) before (a) and after used (b). The diffraction peaks of MgAl<sub>2</sub>O<sub>4</sub> are marked with asterisk.



Fig. 4. Dependence of the conversion of CO on the loading of FeRu nanoparticles.

has great influence on the catalytic activity. As potassium oxide concentration increases from 0 to 6.0 wt%, the catalytic activity get a rapid rise from 2.5% to 87.3%. And then the catalytic activity decreases with further increasing the content of potassium. The  $CO_2$  selectivity increases from 46% to 99% when the potassium oxide concentration increasing from 0 to 4.0 wt%, and reaches 100% with further increase of potassium loading. Thus, an optimum concentration of K<sub>2</sub>O is 6.0 wt% under the comprehensive actions of the above two factors. Besides the effects of property of support, the metal crystallite size, the metal dispersion and the nanoparticles-support interaction may have influence on the activity and selectivity of the supported catalysts.

The catalytic activities of catalysts FeRu/MA with Fe/Ru molar ratio 1.5:1, 1:1 and 0.5:1, FeRu/MA(im), Fe/MA and Ru/MA as a function of reaction temperature are plotted in Fig. 6. The activity of catalyst FeRu/MA increases slowly when the reaction temperature increasing from 120 to 235 °C, and then there is an abrupt increase in the catalytic activity when the reaction temperature increasing from 235 to 265 °C. The CO conversion on catalyst FeRu/ MA at 300 °C is obviously higher than that over monometallic catalysts Fe/MA and Ru/MA. The comparison clearly indicates that the bimetallic catalyst has much higher activity for water-gas shift reaction due to the synergistic effect between iron and ruthenium. The unique catalytic properties for water-gas shift reaction are due to the unique electronic and atomic structures of the bimetallic surfaces, which are quite different from those of the pure metals. It is interesting to compare the activity of catalyst FeRu/MA with that of the catalyst FeRu/MA(im). By comparison, it is evident that the catalyst prepared by colloid method is superior in catalytic activity than the catalyst prepared by impregnation method. This can be attributed to the fact that not all of iron and ruthenium species in catalyst FeRu/MA(im) can form alloy particles.



Fig. 5. Dependence of the CO\_2 selectivity and CO conversion on the loading of K\_2O The reaction temperature is 265  $^\circ C.$ 



Fig. 6. Dependence of the conversion of CO on the reaction temperature over catalyst Fe/MA (a), Ru/MA (b), FeRu/MA(im) (c), FeRu/MA with Fe/Ru 1.5:1 (d), FeRu/MA with Fe/Ru 0.5:1(e) and FeRu/MA with Fe/Ru 1:1 (f).

The catalyst FeRu/MA with Fe/Ru molar ratio 1:1 shows superior catalytic activity than catalysts with Fe/Ru molar ratio of 1.5:1 and 0.5: 1(see Fig. 6). The electronic properties of bimetallic nanoparticles have close relationship with their compositions. It has been reported that the carbon nanotubes can be synthesized from CoMo nanoparticles with different compositions and the catalyst activity can be modulated by changing the Mo content [29]. The author suggested that this phenomenon is related to the production rate of carbon atoms as Mo is inferior to Co in respect of adsorption and decomposing CO to release carbon atoms. In the present study, this would be consistent with the adsorption of CO being an important factor and it is possible that the composition may influence the catalyst activity. However, more detailed study is needed to elucidate the relationship between the properties of nanoparticles and their catalytic activity.

In conclusion, Fe–Ru bimetallic nanoparticles with different diameters and compositions have been prepared by a microwave assisted polyol method. Most of the bimetallic nanoparticles appeared to be single crystals based on the results of HRTEM. The bimetallic nanoparticles were loaded onto MgAl<sub>2</sub>O<sub>4</sub> and tested for water-gas shift reaction. The supported catalyst shows very high catalytic activity due to the synergistic effect between iron and ruthenium and the optimum loading of FeRu nanoparticles was 1.0 wt%. The compositions of nanoparticles have influence on the catalysts activity, and catalyst with Fe/Ru molar ratio 1:1 gave the best result. Potassium can enhance the CO selectivity of catalysts significantly besides increasing the catalysts activity, and the optimum content of  $K_2O$  was 6.0 mol%.

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