



# Rh-Fe alloy derived from $\text{YRh}_{0.5}\text{Fe}_{0.5}\text{O}_3/\text{ZrO}_2$ for higher alcohols synthesis from syngas

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## ARTICLE INFO

### Keywords:

Higher alcohols synthesis  
Ethanol  
Rhodium  
Iron  
Perovskite-type oxide

## ABSTRACT

Traditional Rh-Fe catalysts usually exhibit high alkane or methanol selectivity due to the existence of mono iron and rhodium in the catalysts, and thus the selectivity to higher alcohols is low. To overcome this problem, in this work,  $\text{YRh}_{0.5}\text{Fe}_{0.5}\text{O}_3$  with perovskite structure was loaded on  $\text{ZrO}_2$  by using the citrate complexing method and used for higher alcohols synthesis. Compared with  $\text{RhO}_x/\text{ZrO}_2$ ,  $\text{YRhO}_3/\text{ZrO}_2$  and  $\text{Rh-FeO}_x/\text{ZrO}_2$ , the prepared  $\text{YRh}_{0.5}\text{Fe}_{0.5}\text{O}_3/\text{ZrO}_2$  exhibited better activity and higher selectivity to higher alcohols, the mass fraction of higher alcohols in the total alcohols is more than 80%, especially ethanol occupied 74%. The high selectivity and activity of  $\text{YRh}_{0.5}\text{Fe}_{0.5}\text{O}_3/\text{ZrO}_2$  are attributed to the formation of the homogeneous and highly dispersed Rh-Fe alloys.  $\text{YRh}_{0.5}\text{Fe}_{0.5}\text{O}_3/\text{ZrO}_2$  also showed very good stability. More importantly, this preparation scheme can be extended for the preparation of other multi-component nano alloy catalysts.

## 1. Introduction

As good gasoline additives and substitutes for fossil fuels, higher alcohols which refer to alcohols that have two or more carbon atoms in its molecular formula, have attracted lots of attentions over the past decades. Using syngas which can be derived from biomass or coal to produce these alcohols is an excellent technology road-map [1]. Not only because of that the raw materials are cheap and surplus, but also it was environment-friendly [2]. Catalysts exhibiting high activity and selectivity to higher alcohols are essential for higher alcohols synthesis (HAS) [3].

Rh-based catalysts are attractive owing to their excellent selectivity to ethanol for HAS. However, unprompted Rh nanoparticles (NPs) supported on generally used common supports, such as  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ , mainly produce methane [4]. Various promoters have been investigated for their different promoting effect, among which, iron is particular effective for suppressing methane generation and enhancing the selectivity to  $\text{C}_{2+}$  alcohols (especially to ethanol) [5,6]. For iron promoted Rh catalysts, the formation of bimetallic Rh-Fe alloys is vital to ethanol generation [7–9].

Rh-Fe alloy favors the formation of higher alcohols, while separated mono Fe and Rh generate hydrocarbons. In general, increasing Fe concentration would result in the increase of ethanol selectivity through the formation of Fe-rich alloy. However, the excess of Fe oxides would suppress the active sites of Rh, resulting in a significant drop in CO conversion [10,11]. Usually, Rh-Fe catalysts are prepared

according to the impregnation method. The formation of Rh-Fe alloys is restricted a lot as using impregnation method, therefore traditional catalysts cannot get both high activity and high selectivity to oxygenates, due to that the separated irons favor the formation of hydrocarbons [12–14]. Preparing supported Rh-Fe alloy NPs is still a challenge for the Rh-Fe based catalysts.

Perovskite-type oxides are general abbreviated as  $\text{ABO}_3$ , where A represents a lanthanide and/or alkaline earth metal ion and B is a transition metal ion [15]. Both Rh and Fe elements can be used as the B-site cations to form a perovskite-type oxide [16,17]. By doing this, Rh and Fe elements could disperse closely and uniformly, which would enhance the formation of Rh-Fe alloys.

In this work,  $\text{YRh}_{0.5}\text{Fe}_{0.5}\text{O}_3$  with perovskite structure have been loaded on  $\text{ZrO}_2$  by a simple citrate complexing method and its catalytic performance for HAS was investigated. In  $\text{YRh}_{0.5}\text{Fe}_{0.5}\text{O}_3/\text{ZrO}_2$ , Rh and Fe existed in one molecular, during reaction the formation of Rh-Fe would be favored; meanwhile, due to the high surface area of  $\text{ZrO}_2$ , Rh-Fe would be highly dispersed on  $\text{ZrO}_2$ . As comparison,  $\text{RhO}_x/\text{ZrO}_2$ ,  $\text{YRhO}_3/\text{ZrO}_2$ ,  $\text{Rh-FeO}_x/\text{ZrO}_2$  catalysts were also prepared.

## 2. Experiment

### 2.1. Catalyst preparation

$\text{ZrO}_2$  support was prepared according to the precipitation method as

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<http://dx.doi.org/10.1016/j.cattod.2017.05.057>

Received 25 November 2016; Received in revised form 8 May 2017; Accepted 19 May 2017  
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reported in the literature [18].  $\text{YRh}_{0.5}\text{Fe}_{0.5}\text{O}_3$  was loaded on  $\text{ZrO}_2$  support according to the citrate complexing method [19,20]. Briefly,  $\text{ZrO}_2$  was impregnated with an aqueous solution of yttrium, iron and rhodium nitrate at a molar ratio of 1:0.5:0.5, in which citric acid was in 140% moles of the total cations and glycol was in 20% moles of the citrate acid. After staying overnight, the resulting sample was dried at 120 °C for 24 h, and then calcined at 400 and 700 °C for 2 and 5 h, respectively, at a heating rate of 2 °C  $\text{min}^{-1}$ . For comparison,  $\text{RhOx}/\text{ZrO}_2$ ,  $\text{YRhO}_3/\text{ZrO}_2$  and  $\text{Rh-FeOx}/\text{ZrO}_2$  were also prepared with the same method. The amount of rhodium loading is 2 wt.% in the calcined catalysts.

## 2.2. Catalyst characterization

Temperature programmed reduction (TPR) tests were performed on a Thermo-Finnigan instrument. In each run, 50 mg of the catalyst was loaded into a quartz tube reactor and pretreated in 5%  $\text{H}_2/\text{Ar}$  to remove the air in the reactor. Then, the catalyst was heated from room temperature to 850 °C with a heating rate of 10 °C  $\text{min}^{-1}$  in a 5%  $\text{H}_2/\text{Ar}$  flow at a flow rate of 50  $\text{cm}^3 \text{min}^{-1}$ .

Transmission electron microscopy (TEM) experiments were conducted on a JEOL JEM-2100F microscope field-emission scanning electron microscope. After ultrasonic dispersion of the catalysts in absolute ethanol the samples were deposited on nickel grids with a holey carbon film support. The particle diameter distribution analysis based on TEM images was achieved by the nano-measurer tools.

X-ray diffraction (XRD) patterns were collected on a Bruker D8-Focus X-ray diffractometer with Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ). The spectra were obtained between the  $2\theta$  range of 20–70° at a scanning speed of 5°  $\text{min}^{-1}$ .

The elemental electronic states of the catalyst surface were investigated by using X-ray photo spectroscopy (XPS). Before test, the catalyst was reduced at 200 °C for 3 h in pure  $\text{H}_2$ , then lowered the temperature of the reactor to room temperature, and then sealed the reactor. The sample in the sealed reactor was transferred into the XPS chamber in a nitrogen box to avoid oxidation. The measurements were carried out on a Physical Electronics (PHI) spectrometer model 590. The photoelectron kinetic energy was measured by Omni Focus III spherical capacitance analyzer (SCA). Magnesium anode was used as the source of X-ray radiation ( $\text{MgK}\alpha$ : 1253.6 eV). The pressure in the analysis chamber was maintained between  $10^{-8}$  and  $10^{-9}$  Torr during the measurements. The binding energies were corrected utilizing the reference binding energy (BE) of adventitious carbon C1 s at 284.8 eV. The spectra from the regions related to Zr3d, Y3d, Rh3d, C1s, and O1s core levels were recorded and analyzed using “Auger-Scan” analysis software developed by RBD Instruments.

Thermal analysis of thermogravimetric (TG) was performed on a DTG-50/50H from Shimadzu Corporation from room temperature to 900 °C with a heating rate of 10 °C  $\text{min}^{-1}$  and in flowing air. 5.0–10.0 mg of catalyst was used. The total weight loss is determined by the following equation

$$(W_1 - W_2)/W_1 \times 100\%$$

where  $W_1$  is the weight of the reacted catalyst before TG test, and  $W_2$  is the weight of the reacted catalyst after the TG test.

## 2.3. Catalytic performance

Catalytic performance tests were carried out in a stainless-steel continuous fixed-bed flow micro-reactor. 800 mg of catalyst was used in each run. The catalysts were reduced at 200 °C for 3 h with a  $\text{H}_2$  flow rate of 30  $\text{mL min}^{-1}$ . Subsequently, the reactor was cooled to room temperature, and the pressure was increased to 4 MPa by feeding the syngas mixture ( $\text{H}_2/\text{CO}/\text{N}_2 = 8:4:1$ , where  $\text{N}_2$  was used as the internal standard gas to analyze the composition of the off-gas) from the

pressurized manifold. The gas hourly space velocity (GHSV) was set at 3000  $\text{h}^{-1}$  via adjustment of an individual mass flow controller. The reaction was maintained for 20 h at 290 °C with temperature ramping rate around 5 °C  $\text{min}^{-1}$ . Gas chromatograph with two packed columns was used to analyze the products.  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{N}_2$  among the gas products were separated online using a TDX-01 packed column (2 m) connected to the TCD detector. Hydrocarbons and the condensed liquid products were analyzed off-line using a Porapak Q column (3 m) connected to an FID detector.

$\text{CO}$  conversion (%) and the product selectivities (%) were calculated according to the following equations: Conversion (%) =  $\frac{\sum n_i}{M_i} \times 100/M_{\text{CO}}$  and selectivity =  $n_i M_i / \sum n_i M_i$ . Where  $n_i$  is the number of carbon atoms in product  $i$  (hydrocarbon,  $\text{CO}_2$ , Alcohol),  $M_i$  is the mole percent of product  $i$  measured, and  $M_{\text{CO}}$  is the mole percent of carbon monoxide in the feed.

## 3. Results and discussions

### 3.1. XRD

The powder X-ray diffraction patterns of the calcined catalysts are shown in Fig. 1. All of the diffraction peaks, except the weak peaks at  $2\theta \approx 38.6^\circ$  marked with dash line, are attributed to monoclinic  $\text{ZrO}_2$ . No peaks corresponding to oxide of Rh, Y or Fe could be detected.

To confirm the existence of  $\text{YRhO}_3$  and  $\text{YRh}_{0.5}\text{Fe}_{0.5}\text{O}_3$  on the surface of  $\text{ZrO}_2$ , catalysts with higher Rh content (4 wt.%) were prepared [21], the XRD patterns are shown in Fig. 1c and e. The samples with 4 wt.% Rh loading exhibited obvious diffraction peaks at  $2\theta \approx 38.6^\circ$ , which are attributed to perovskite-type oxides of  $\text{YRhO}_3$  and  $\text{YRh}_{0.5}\text{Fe}_{0.5}\text{O}_3$ , see the enlarged pattern of the inset in Fig. 1. Depending on general experiences, only agglomerates of metal nanoparticles with size of higher than 4–5 nm can be detected by XRD. As metal ions are easily dispersed on the surface of  $\text{ZrO}_2$  because of the existence of  $-\text{OH}$  groups [22], agglomerates of metal nanoparticles need a higher capacity. The XRD results indicate that  $\text{YRhO}_3$  and  $\text{YRh}_{0.5}\text{Fe}_{0.5}\text{O}_3$  were successfully loaded on  $\text{ZrO}_2$ , and the perovskite-type oxides were highly dispersed on  $\text{ZrO}_2$ . For samples b and d, the diffraction peaks corresponding to perovskite structure are too weak to be clearly seen, due to their low loading content.

### 3.2. TPR

Fig. 2 shows the TPR results of the samples. It can be seen that all samples exhibit two obvious  $\text{H}_2$ -consuming peaks, one with a shoulder appearing at low temperature (150 °C) exhibits high amount of  $\text{H}_2$

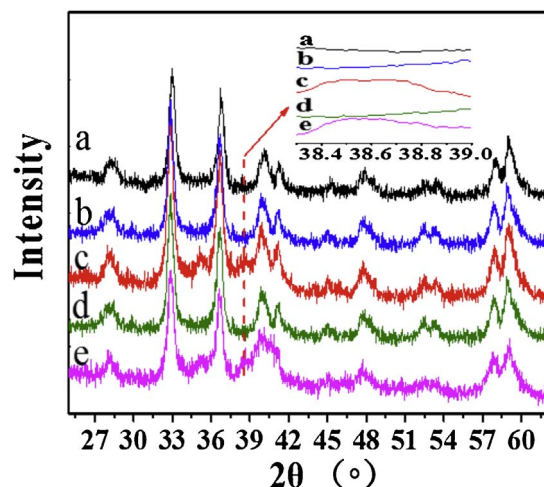


Fig. 1. XRD patterns of (a)  $\text{RhOx}/\text{ZrO}_2$ , (b)  $\text{YRhO}_3/\text{ZrO}_2$ , (c)  $\text{YRhO}_3/\text{ZrO}_2$  (4% Rh), (d)  $\text{YRh}_{0.5}\text{Fe}_{0.5}\text{O}_3/\text{ZrO}_2$  (e)  $\text{YRh}_{0.5}\text{Fe}_{0.5}\text{O}_3/\text{ZrO}_2$  (4% Rh).

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