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Effect of impregnation sequence of Ce promoter on the microstructure and performance of Ce-promoted Rh-Fe/SiO_2 for the ethanol synthesis

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ABSTRACT

Ce-promoted Rh-Fe/SiO_2 catalysts were prepared using different impregnation methods and evaluated in syngas conversion to ethanol. The catalyst prepared by co-impregnation method (Rh-Fe-Ce/SiO_2) showed higher ethanol selectivity than those prepared by sequential impregnation methods (Ce/Rh-Fe/SiO_2 and Rh-Fe/Ce/SiO_2). Characterization results indicated that when Ce was co-impregnated with Rh and Fe, it had higher dispersion and inhibited the reduction of Rh oxides. Additionally, the reduction of CeO_2 was promoted. The Rh-Fe-Ce/SiO_2 catalyst exhibited the highest spatial association between Rh and Ce, which was responsible for the highest ethanol selectivity.

1. Introduction

Ethanol can be used as a fuel additive or as a hydrogen carrier, and is widely recognized as a potential fuel alternative. The selective synthesis of ethanol from syngas has attracted academic and industrial interest since the 1980s. However, the process has not been commercially implemented due to the poor product yield and low selectivity using most known catalysts. Hence much effort has been devoted to developing efficient and selective catalysts for synthesizing ethanol in the past decades.

The superior catalyst for ethanol synthesis from syngas is Rh-based catalyst. However, unpromoted Rh nanoparticles supported on the most used SiO_2 support show low activity and poor selectivity to ethanol. In comparison, the addition of promoters greatly improves the catalytic performance. Thus, a large amount of scientific work has been done to search for the optimum promoter, or combination of promoters [1–6]. Ceria and iron have been studied for enhancing ethanol synthesis from syngas, and have shown interesting promoting effect on Rh for higher ethanol yield [7–14]. Ceria might stabilize Rh^+ [8] and the formyl species [13], and iron was reported to stabilize absorbed CO [11] and enhance hydrogenation [14]. Although their promoting mechanism is still unclear, it is believed that the Rh-promoter interface plays an important role in creating the active sites for ethanol synthesis.

On the other hand, less attention has been focused on the effect of preparation methods for introducing the promoters. Different preparation methods might affect the Rh-promoter interaction and the dispersion of different components, thus affect the catalytic performance. For example, Yu et al. [15] and Wang et al. [16] found the sequences of introducing the Fe promoter had great effect on the activity and selectivity of the catalysts. Borer et al. [17] also found the impregnation sequence affected the performance of lanthana promoted Rh/SiO_2 catalysts.

However, most studies focused on bi-component catalysts. To reveal whether the similar phenomenon occurs for tri-component catalyst, Ce-promoted Rh-Fe/SiO_2 catalysts were prepared by co-impregnation and sequential impregnation methods. The obtained samples were investigated for CO hydrogenation to ethanol. The influence of impregnation sequences on the microstructure of the catalysts was also studied in detail.

2. Experimental

2.1. Catalyst preparation

$Rh(NO_3)_3$ solution (97.25 g/L, Kunming Institute of Precious Metals), $Fe(NO_3)_3{\cdot}9H_2O$ (98.5%, Sinopharm Chemical Reagent Co., Ltd.), $Ce(NO_3)_3{\cdot}6H_2O$ (99.0%, Sinopharm Chemical Reagent Co., Ltd.), and silica gel (Haiyang Chemicals Plant) were used in catalyst preparations. Silica gel was first crushed and sieved into the

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size of 40–60 mesh. The sieved silica gel was washed sequentially with HNO_3 and deionized water, and then dried in air at 110 °C overnight before being used as a support (BET surface area after pretreatment was 403 m^2/g).

For the catalysts referred to as Rh-Fe, Rh-Ce and Rh-Fe-Ce, silica gel was impregnated with a requisite amount of pre-mixed $Rh(NO_3)_3$, $Fe(NO_3)_3$ and/or $Ce(NO_3)_3$ solution. Rh-Fe/Ce represents a catalyst prepared by sequential impregnation method. The silica gel was first impregnated with $Ce(NO_3)_3$ solution, then the obtained sample was impregnated with pre-mixed $Rh(NO_3)_3$ and $Fe(NO_3)_3$ solution. Ce/Rh-Fe represents a catalyst prepared by reverse sequential impregnation method. The catalyst was prepared using the same procedure as sequential impregnation method, except that the silica gel was first impregnated with pre-mixed $Rh(NO_3)_3$ and $Fe(NO_3)_3$ solution, and then impregnated with $Ce(NO_3)_3$ solution. Following each impregnation, the catalyst was dried at 110 °C for 12 h and calcined at 450 °C in air for 3 h.

2.2. *Catalyst evaluation*

CO hydrogenation was carried out in a fixed bed micro-reactor under 290 °C, 3.0 MPa ($H_2/CO = 2$) and a constant GHSV of ca. 5,000 h^{-1}. In a typical experiment, the catalyst (1 ml) diluted with 2 ml of inert silica sand was packed between two plugs of quartz wool in the middle of the reactor. The reaction temperature was detected by a thermocouple in the middle of the catalyst bed. Prior to the reaction, the catalyst was reduced in situ in a pure H_2 flow at 300 °C for 1 h, with a ramp of 2 °C/min. Then the catalyst was cooled down to 290 °C and shifted into syngas ($H_2/CO = 2$). The product gas went through a cold trap, and then analyzed on-line by an Agilent 7890A gas chromatograph. The aqueous product collected in the condenser was analyzed off-line by Agilent 7890A gas chromatograph using a FID detector and 1-pentanol as an internal standard. The CO conversion was calculated according to the following equations [2]:

$$\mathrm{COconversion}[\%] = \left(\sum \mathrm{Ai}\cdot\mathrm{Bi}/\mathrm{Bco}\right) \times 100$$

where Ai is the carbon number of ith product, Bi is the percentage of product i detected, and Bco is the percentage of carbon monoxide in the syngas feed. The selectivity of the ith product was calculated based on the carbon efficiency as follows [2]:

$$\mathrm{Selectivity}[\%] = \frac{(\mathrm{Ai}\cdot\mathrm{Ci})}{(\Sigma\mathrm{Ai}\cdot\mathrm{Ci})} \times 100$$

where Ci is the molar concentration of the ith product. The carbon balance of the different experiments was 100 ± 2%.

2.3. *Catalyst characterization*

X-ray diffraction (XRD) measurements were performed on a PANalytical Empyrean diffractometer with a monochromatic Cu Ka radiation source ($\lambda = 0.15406$ nm) at 55 mA and 60 kV. The 2θ diffractograms were recorded between 5 and 80° with a step size of 0.04°. The N_2 adsorption–desorption isotherms were measured at the liquid nitrogen temperature in a Quantachrome NOVA2200e instrument. Prior to analysis, the samples were degassed under vacuum at 200 °C for at least 2 h. The metal content of the catalysts was determined by inductively coupled plasma-optical emission spectrometer (ICP-OES). X-ray photoelectron spectra (XPS) were recorded using a Thermo Scientific ESCALAB 250Xi Spectrometer equipped with an Al Kα X-ray source. The binding energy was corrected using C(1 s) at 284.6 eV. The H_2 temperature programmed reduction (H_2-TPR) tests were carried out using a QuantaChrome CHEMBET Pulsar adsorption instrument coupled with a TCD detector in a flow system. Electron micrographs of the samples were acquired on a JEOL JEM 2100F apparatus, which was equipped with a high angle-annular dark field detector for scanning transmission electron microscopy (HAADF-STEM) technique, and an X-Ray energy dispersive spectroscopy (XEDS) detector. Fourier transform infrared spectroscopy (FT-IR) spectra were collected with a Nicolet 6700 spectrometer equipped with a MCT-A detector cooled by liquid nitrogen and a high pressure/high temperature cell from Specac.

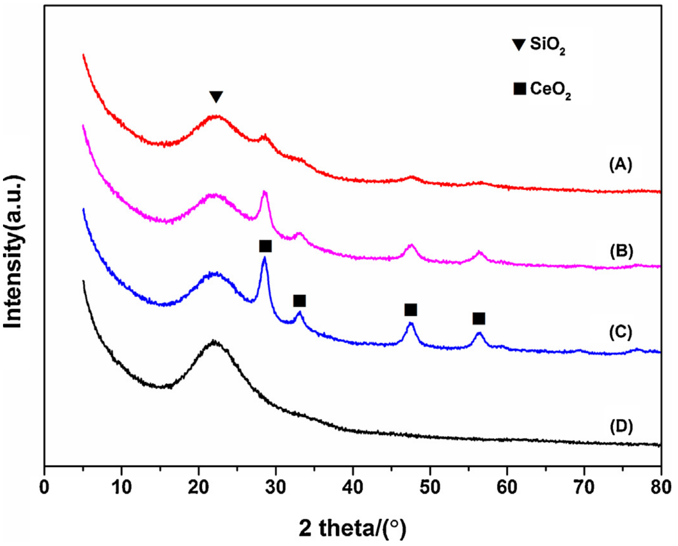

Fig. 1. XRD profiles of Rh-based catalysts for (A) Rh-Fe-Ce; (B) Ce/Rh-Fe; (C) Rh-Fe/Ce; (D) Rh-Fe.

3. Results and discussion

3.1. *XRD, N_2 adsorption and elemental analysis results*

The XRD patterns of Rh-based catalysts are shown in Fig. 1. A very broad peak at 2θ of ca. 22.0° was clearly observed on all catalysts, which can be ascribed to amorphous SiO_2 (JCPDS 29-0085). The typical diffraction peaks of cubic CeO_2 (JCPDS 34-0394) were observed at $2\theta = 28.6°$, 33.1°, 47.5° and 56.3° for all Ce-containing samples. The lowest intensities and broadest widths of these peaks for Rh-Fe-Ce indicated that it had smaller crystallite size of CeO_2 than Ce/Rh-Fe and Rh-Fe/Ce. The average crystallite sizes of CeO_2 listed in Table 1 were determined from the Scherrer equation. No diffraction peaks attributed to Rh and Fe species were observed in any of the samples, which implied that the Rh and Fe species were highly dispersed, possibly owing to their low contents.

The textural properties of the catalysts were characterized and the results are given in Table 1. Compared with SiO_2 support (403 m^2/g), the Rh-Fe supported catalyst showed a slight decrease on BET surface area. While the Rh-Fe-Ce showed a decrease of 31 m^2/g and the other two catalysts, Ce/Rh-Fe and Rh-Fe/Ce showed surface areas about 39–43 m^2/g lower than SiO_2 support. Compared with Rh-Fe, only minor decreases were observed in total pore volume of the Ce-containing catalysts, while no changes were observed in the average pore diameter. The Rh, Fe, and Ce contents in all samples were close to their nominal values of 2.0, 0.5, and 3.0 wt%, respectively.

As expected, the surface area and pore volume of the supports were decreased owing to the blockage of narrow pores by the introduction of Rh, Fe and Ce species, and the extent was dependent on the impregnation sequence. It is known that the pH of the impregnating solution and the zero charge point of the support greatly affect the interaction between the metal precursor