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Plasma-assisted preparation of Fe–Cu bimetal catalyst for higher alcohols synthesis from carbon monoxide hydrogenation

Hui Zhang, Wei Chu *, Huiyuan Xu, Jun Zhou

Department of Chemical Engineering, Sichuan University, Chengdu 610065, China

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ABSTRACT

Plasma-assisted Fe–Cu/SiO_2 catalysts were prepared by impregnation technique and characterized by X-ray diffraction (XRD), nitrogen adsorption and desorption isotherms, X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (H_2-TPR) techniques. Catalytic performances for carbon monoxide hydrogenation to higher alcohols were carried out in a fixed-bed reactor at the conditions of T = 300 °C, P = 5 MPa, H_2/CO = 2, GHSV = 6000 ml/g_{cat} h. Plasma-promoted Fe–Cu bimetal catalyst (FeCuSi-PC) possessed much better catalytic performances than those of conventional sample in the selective hydrogenation of carbon monoxide. XRD and XPS analysis suggested that the plasma assistance in the catalyst preparation remarkably diminished the particle size, improved the catalyst dispersion, and issued an exposure of more copper and iron species on the catalyst surface. The mechanism of plasma on catalyst crystallize size was also discussed.

1. Introduction

Selective conversion of syngas (mixture of CO and H_2) to valuable chemicals has attracted more and more attentions [1–5]. Higher alcohols could be used as suitable octane boosters. The efficiency of syngas conversion could be improved by novel efficient catalyst design [6–13]. Several approaches have been issued for developing new efficient catalysts for carbon monoxide hydrogenation to higher alcohols. Fischer-Tropsch elements (cobalt, iron) modified copper [14–18] and molybdenum [19] based catalysts were widely developed for higher alcohols synthesis. Highly dispersed Co–Cu catalyst for CO hydrogenation to higher alcohols was evidenced by Fierro et al. [14] and de Aquino and Cobo [15]. The results revealed that highly dispersed cobalt interacting with copper facilitated the migratory CO insertion into a metal–alkyl bond, which was responsible for high selectivity of higher alcohols. The incorporation of Fe into $CuMnZrO_2$ catalyst was also reported for higher alcohols synthesis [16–18]. It could lead to an increase in the content of C_2^+OH.

Glow discharge plasma, as an unconventional technique, demonstrates important effects on the catalyst preparations [20–25]. Novel Pd/HZSM-5 catalyst prepared by the glow discharge plasma treatment with a further thermal oxidation led to a much higher methane conversion (nearly two times) than that of the catalyst prepared by conventional method [22]. As the glow discharge plasma could produce a large number of non-equilibrium highly activated species, there were higher metallic dispersion and lattice defects for the plasma-treated catalyst, which attributed to excellent catalytic performances.

In our recent works, glow discharge plasma technique was extensively applied in a series of catalyst preparations, and some promising results were presented [23–27]. Plasma activation of a Ni/Al_2O_3 catalyst was efficient for methane conversion to syngas [24]. Higher methane conversion was attributed to a better dispersion in Ni/Al_2O_3 catalyst treated by glow plasma. Comparing to the result of conventional sample, carbon monoxide conversion of plasma-treated Fischer-Tropsch cobalt catalyst increased significantly, with a similar selectivity.

In this work, the introduction sequence effects of glow discharge plasma in catalyst preparation process were investigated on the properties of Fe–Cu catalysts for higher alcohols synthesis from CO hydrogenation. Plasma-promoted FeCuSi catalysts were characterized with XPS, XRD, CO-TPD, BET, and H_2-TPR techniques.

2. Experimental

2.1. Catalyst preparation

Fe–Cu catalysts were prepared by impregnation using silica support (60–100 mesh, Qingdao Ocean Chemical Plant, China), with the mixture solution of $Cu(NO_3)_2{\cdot}3H_2O$ and $Fe(NO_3)_3{\cdot}6H_2O$. Catalyst precursor was obtained by drying at 110 °C for 16 h in air. Then glow discharge plasma was introduced at different stage catalyst preparation for assistance. Three catalyst samples were

* Corresponding author.
E-mail addresses: zhanghui8047@yahoo.com.cn (H. Zhang), chuwei65@yahoo.com.cn (W. Chu).

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obtained as follows: (a) the dried precursor was directly calcined at 350 °C for 3 h in the air and denoted as FeCuSi-C; (b) the dried precursor was firstly calcined at 350 °C for 3 h in the air, then the calcined catalyst was put into the discharging tube for decomposed and reduction, in the N_2 atmosphere and then H_2 atmosphere for each 45 min by glow discharge plasma. The discharge parameters were as follows: frequency 13.56 MHz, discharge voltage 100 V and anodic current 50 mA. This sample was nominated as FeCuSi-CP; (c) the precursor was firstly treated by glow discharge plasma with the similar plasma conditions for FeCuSi-CP catalyst, and then the plasma-treated sample was calcined at 350 °C for 3 h in the air, the final sample was nominated as FeCuSi-PC. Copper and ion content were 20 and 7.2 wt.% in each sample.

2.2. Catalyst characterizations

The texture properties were measured by the N_2 adsorption/desorption isotherms, using a Quantachrome Nova 1000e apparatus at liquid nitrogen temperature. Samples were degassed at 300 °C for 3 h prior to analysis.

X-ray diffraction (XRD) measurements were performed on a Philips X'pert MPD X-ray diffractometer equipped with a graphite monochromator and Cu Kα (40 kV, 40 mA) radiation. The average particle size was calculated using the Sherrer's equation.

$$d = \frac{k\lambda}{B\cos\theta}\frac{180^\circ}{\pi}$$

where d is the mean crystallite diameter, λ the X-ray wave length (1.54056 Å), and B is the full width half maximum (FWHM).

X-ray photoelectron spectra (XPS) experiments were tested on the XSAM800 spectrometer with an Al anode for Ka (1486.6 eV) radiation. Charging effects were corrected by adjusting the binding energy of C1s peak from carbon contamination to 284.6 eV.

CO-TPD experiments were conducted using the same instrument as the TPR. The sample was reduced with H_2 at 350 °C for 1 h, cooled down in flowing N_2 to 50 °C, and then adsorbed CO for 30 min. After the sample was purged with N_2, CO-TPD was performed at a heating rate of 10 °C/min.

Temperature-programmed reduction (H_2-TPR) was carried out in a quartz reactor at atmospheric pressure. Fifty milligrams sample was loaded in the middle of the reactor tube, flushed with N_2 at 100 °C for 1 h. Then N_2 was replaced and stabilized by the reductive gas (5% H_2/N_2) at a flow rate of 30 ml/min. The temperature of the reactor was augmented linearly from 100 to 700 °C with a ramp of 10 °C/min by a temperature-programmed controller. The effluent gas was analyzed by a thermal conductivity detector (TCD), recorded by a computer work-station.

2.3. Catalytic activity measurements

The activity tests for selective hydrogenation of carbon monoxide were carried out in a fixed-bed micro-reactor (stainless steel, 300 mm length). Sample (500 mg) was loaded into the reactor, and reduced by pure hydrogen under atmospheric pressure at 300 °C for 5 h. Then syngas [$V(H_2)/V(CO) = 2$] was introduced and catalytic reaction was carried out at 300 °C, 5.0 MPa, 6000 ml/g_{cat} h. Liquid products were captured using an ice-water bath, and analyzed by a gas chromatograph (GC 112A) equipped with a SE-30 capillary column (0.33 mm i.d. and 30 m length) and a flame ionization detector (FID). Effluents such as H_2, CO, CO_2 and CH_4 were separated by TDX-601 packed column and monitored online by a thermal conductivity detector (TCD) equipped on a gas chromatograph (SC-200). Hydrocarbons such as CH_4 and C_2H_6 were analyzed using a DNBM-ODPN packed column and an FID GC.

3. Results and discussion

3.1. Surface and structural properties of catalysts

The XPS spectra for Cu2p and Fe2p of FeCuSi-C, FeCuSi-PC catalysts are displayed in Fig. 1. From the XPS spectra of Cu2p, for the FeCuSi-C catalyst, the $Cu2p_{3/2}$ and $Cu2p_{1/2}$ binding energies at 933.5 and 953.4 eV, could be ascribed to the presence of Cu^{2+} species. In comparison with those of FeCuSi-C catalyst, the $Cu2p_{3/2}$ and $Fe2p_{3/2}$ binding energies of FeCuSi-PC, respectively, shifted 0.9 and 0.7 eV toward high energy region. XPS spectra indicated that the synergic interaction of iron and copper was improved due to the introduction of plasma technique. As it was well-known, the higher alcohol synthesis required two active sites for undissociative and dissociative CO [1,3]. Dissociated CO on iron active sites coordinated with adsorbed CO on reductive $Cu^{\delta+}$ ($0 < \delta < 2$) on the catalyst surface, which was responsible for the formation of higher alcohols synthesis.

The copper and iron contents on the catalyst surface calculated from the XPS spectra, is shown in Table 1. The introduction of plasma resulted in remarkable varieties of relative concentrations of Cu and Fe elements. The results of the semi-quantitative calculation showed that the ratio of Cu/Si on the surface of FeCuSi-PC was about two times of that of conventional FeCuSi-C catalyst and the largest amount of Fe element was enriched on the surface of FeCuSi-PC catalyst. It was suggested that plasma could apparently improve the number of copper and iron exposed on the surface of catalyst assisted by plasma.

The CO-TPD profiles of the catalyst samples are shown in Fig. 2. Two desorption peaks appeared and little difference in the area and

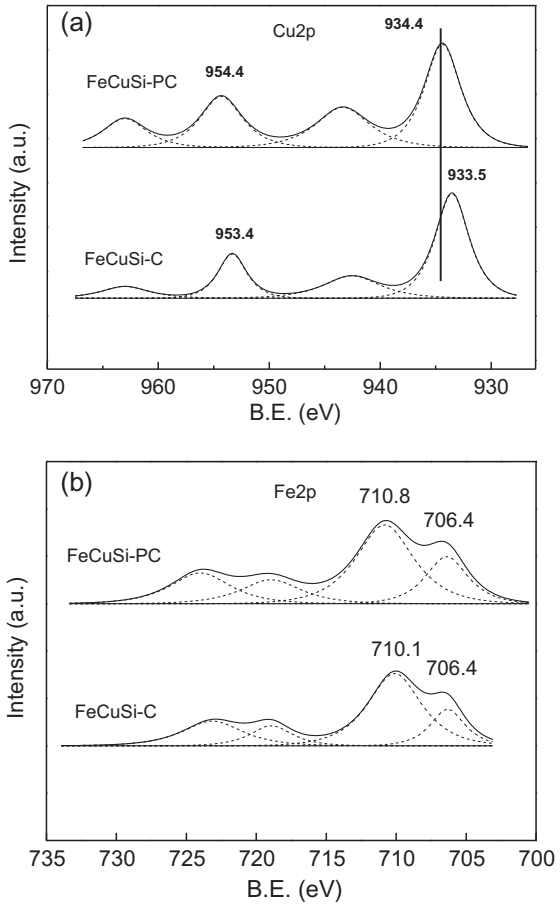

Fig. 1. Cu2p and Fe2p XPS spectra of Fe–Cu bimetal catalysts.