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Structure evolution of spinel Fe-M^{II} (M = Mn, Fe, Co, Ni) ferrite in CO hydrogeneration

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ABSTRACT

The CO hydrogeneration *via* the Fischer-Tropsch reaction (FTO) has been carried out over spinel bimetallic Fe-M^{II} (M = Fe,Mn,Co,Ni) ferrite. The catalytic performance shows that Fe-Mn ferrite has the highest lower olefin selectivity of 54.5%, while Fe-Ni ferrite has the highest CH_4 selectivity. The initial structure of the ferrite is characterized by scanning electron microscopy, energy-dispersive spectrometry, X-ray diffraction (XRD), and Raman spectroscopy. The structure evolution was also characterized by *in situ* XRD. The results revealed that the doping of a second metal decreases the grain size and microsphere size. Also, the doping of Mn promotes the reduction of $Mn_xFe_{3-x}O_4$ phase to $Mn_xFe_{1-x}O$ phase; however, further reduction of Fe^{2+} in the $Mn_xFe_{1-x}O$ phase is inhibited, while the doping of Co and Ni favors the reduction of $M_xFe_{3-x}O_4$ to alloy phase and metal phase. χ-Fe_5C_2 phase was found for all the spent catalysts, a small ε-Fe_2C phase was also detected from spent Fe-Mn ferrite, and θ-Fe_3C determined to be the principle carbide for the spent Fe-Co sample.

1. Introduction

Lower olefins [ethylene, propylene, and butylenes (C_2-C_4)] are the most essential and primary industrial materials for the production of plastic, rubber, film, etc. [1]. Traditionally, lower olefins are produced by steam cracking of naphtha, dehydrogenation of hydrocarbons, or as by-products of oil-refining processes [2]. However, the oil-reserve crisis has gradually become a heated issue. As is well known, Asia's coal reserves are much greater than those of gas and oil [3]. It is therefore conceivable that developing coal-based syngas to produce lower-olefin products has crucial strategic significance. The conversion of syngas directly to lower-olefin products via Fischer-Tropsch synthesis (FTO), as a direct route without intermediate steps, has proved to be an alternative process to increasing olefin output [4,5].

The advance in FTO has been recently reviewed by Torres Galvis et al. [6]. Generally, the development of high-performance catalysts is still of paramount importance. In the past several decades, the Fischer-Tropsch catalysts based on group-VIII metals such as Fe, Co, Ru, Rh, and Ni have been extensively investigated [7–11]. Iron-based catalysts are widely used for FTO as they are cheap and widely available. They also have high selectivity for olefin and low selectivity for methane, as well as the feasibility of lowering the H_2/CO ratios derived from coal or biomass [12,13]. Moreover, they exhibit high activity for both Fischer-Tropsch synthesis (FTS) and Water-Gas Shift (WGS) reactions [6,14]. However, there are still some areas of dispute in the reaction process when iron-based catalysts are used in CO hydrogenation, such as the phase transformation, reaction mechanism, and active phases. Furthermore, the performance of iron-based catalysts can be significantly affected by many factors, such as supports, promoters, the addition of a second metal, etc.

Many studies have shown that the use of bimetallic catalysts with generated synergistic geometric and electronic effects can improve FTS performances (activity, selectivity, and stability) of Fe-based catalysts. Typical iron-FTS bimetallic Fe-M (M = Co,Ni, and Mn) catalysts have shown excellent performance for FTS [15–17]. Fe-Co catalysts are efficient in producing C_2-C_4 olefins and are stable under a CO/H_2 atmosphere, with only few carbides detected [15,18]. Ni is a well-known methanation catalyst, so it is expected that it would have a negative influence on the O/P ratio [16,17]. Mn can decrease the methane selectivity and promote the formation of olefin [19]. However, in a previous study, most of the precursor is Fe_2O_3, which is obtained by calcination in air. In addition, the catalysts are mainly prepared by co-precipitation. In fact, co-precipitation is the preferred choice for most studies owing to the simple preparation conditions and operational process; however, mixture by co-precipitation is not homogenous enough, and it is difficult to control the shape and size of the final products. In addition, FT is viewed as a structure-sensitive reaction, and the shape and size of the catalysts have significant effects on catalytic

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performance [20]. In recent years, Fe_3O_4 microspheres prepared by the solvothermal method have been used as FTO catalysts [21–23]. The preparation process is simple, environmentally friendly, and the grain size can be adjusted. In addition, the support-free Fe_3O_4 microspheres can overcome any strong metal-support interaction. In this paper, the second metals were doped using one-pot solvothermal method and a series of Fe-based spinel Fe-M^{II} (M = Mn,Fe,Co,Ni) ferrites obtained. The ferrites were used to direction-convert syngas to lower olefins, and the key is focusing on the effect of the doping of second metal on the performance of the reduction and CO hydrogenation.

2. Experiment

2.1. Catalyst preparation

Fe_3O_4 ferrite was prepared through a solvothermal reaction [24,25]. Fe-*M* (M = Mn,Co,Ni) was prepared as follows: Using Fe-Mn ferrite as an example, $FeCl_3·6H_2O$ (analytical reagent (AR), SinoPharm, China) and $MnCl_2·4H_2O$ (AR, SinoPharm, China) were dissolved in ethylene glycol to form a clear solution; the total initial metal-ion concentration was 0.1 M. The nominal content of second doping metal is 33.3% relative to the total metal ions during solvothermal synthesis. After stirring the solution for 1 h, sodium acetate was added, and the mixture was vigorously stirred for 1 h. The mixture was then sealed in a Teflon™-lined stainless-steel autoclave (100 mL capacity). The autoclave was heated and maintained at 200 °C for 8 h, and allowed to cool to room temperature. The products were washed several times, separately with ethanol and with water. They were then collected by magnet and dried at room temperature under vacuum and kept in a vacuum oven. The other two Fe-*M* (M = Co,Ni) ferrites were prepared using the same procedure. The actual content of second doping metal is denoted as *M* (%) determined by ICP and EDS.

2.2. Characterization

2.2.1. Scanning electron microscopy

The morphologies of the samples and the elemental concentrations of the catalysts, as well as elemental distributions, were studied using scanning electron microscopy (SEM) and energy-dispersive X-ray (EDS) spectroscopy. The mean microsphere size was obtained from SEM images. SEM equipped with EDX spectroscopy was performed using a high-resolution field-emission SEM instrument (NOVA Nano SEM450, FEI/ThermoFisher Scientific, USA) under the scanning electron (SE) mode. The accelerating voltage was 3 kV with a working distance of 5 mm.

2.2.2. Inductively coupled plasma spectrophotometer

The element contents of samples were obtained by Inductively Coupled Plasma spectrophotometer (ICP) (Perkin Elmer Avio 500). The 0.10 ~ 0.15 g of sample was dissolved into 3 mL of concentrated HNO_3 (65%) and diluted into 50 mL with deionized water. Subsequently, the solutions were performed on the ICP.

2.2.3. X-ray powder diffraction

X-ray powder diffraction (XRD) analysis was carried out on a diffractometer (D8 Advance, Bruker Corp., USA). Cu $K\alpha$ radiation ($\lambda = 1.5406$) obtained at 40 kV, and 40 mA was used as the X-ray source. The XRD patterns used to calculate the grain size and lattice parameters of the fresh catalyst were obtained with 0.02° as one step, at a scanning rate of 0.24°/min. The intensity of the highest peak is more than 10,000 counts per second (cps). The grain size of the microspheres was calculated with Scherrer's equation using the Fe_3O_4(311) peak at $2\theta = 35.5°$. The lattice parameters were calculated using the Rietveld refinement software TOPAS (Bruker Corp., USA). The XRD patterns of the spent catalyst were obtained with 0.02° as one step, at a scanning rate of 3°/min.

The *in situ* XRD experiments in a H_2 atmosphere were carried out on the same instrument in a reaction chamber (XRK-900, Anton Paar GmbH, Germany). In each XRD experiment, diffraction patterns of the catalyst were recorded within a 2θ range of 10°–80°, at a scanning rate of 10°/min, and the sample was heated in a flow of 3% H_2 in Ar (50 mL/min) up to 623 K at a rate of 5 K/min for 5 h. During this process, the XRD patterns were collected at the pre-specified temperatures.

2.2.4. H_2-temperature-programmed reduction (H_2-TPR)

Prior to the experiment, the sample (50 mg) was purged with Ar (30 ml·min^{-1}) at 428 K for 1 h so that the physically adsorbed H_2O could be removed from the samples. The H_2-TPR experiments were performed using a fixed-bed micro-reactor connected with a thermal conductivity detector (TCD). The temperature was ramped from 303 to 398 K at a rate of 20 K·min^{-1} for 5 min, and the temperature was then ramped to 1098 K at a rate of 10 K·min^{-1} in a 10% H_2/He flow of 50 mL·min^{-1}.

2.2.5. Raman

The laser Raman spectrometer (LabRAM HR, Horiba J.Y., Japan) was equipped with a high-grade microscope (Leica Camera AG, Germany; long working distance objective lens, 50 ×). The sample was placed in the *in situ* cell under the protection of Ar at a flow rate of 30 ml/min. Raman measurements were performed on different sample spots irradiated by a visible 514.5-nm Ar^+-ion laser. The single silicon crystal was used for position correction. The confocal hole was set to 200 mm for all tests. The attenuator (D0.6) was used for the tests to avoid signal overflow and sample degradation. The exposure time was set to 40 s for each spectrum. The scattered light was collected at 180° (back-scattering plane) and detected by a deep-depleted, thermoelectrically cooled, charge-coupled-device (CCD) array detector (1024 × 256 pixels, 26 mm in size).

2.3. Catalytic performance

CO hydrogenation was performed in a stainless-steel, continuous, fixed-bed micro-reactor with a length of 450 mm, inner and external diameter of 6 mm and 9 mm. The catalyst precursor was first reduced at 623 K with H_2 (30 mL·min^{-1}) for 5 h. Ahead of the reaction, syngas at 2.0 MPa was then introduced into the reaction system. The reaction temperature was monitored by a thermocouple inserted into the catalyst bed, and a time-on-stream of 20 h was taken for each measurement. Catalyst screening experiments were usually measured under the following conditions: 533 K; gas hourly space velocity (GHSV) of 4000 h^{-1}; H_2/CO ratio = 1; 25 mg catalyst diluted with 75 mg SiC. The blank test was implemented using SiC, and a less than 0.45% conversion of CO was detected under the same reaction conditions. The products were analyzed using an online gas chromatograph (GC2060 Shanghai Ruimin, China).

3. Results and discussions

3.1. Catalytic performance of Fe-M ferrite

The catalytic performance results of the Fe-*M* catalyst in CO hydrogenation is shown in Table 1. After adding the Fe-*M* catalyst, the CO conversion ratio ranged from 3.3 to 7.0%, implying that the CO hydrogenation is catalyzed. However, the addition of a second metal decreased the conversion slightly, although Fe-Mn, Fe-Co, and Fe-Ni catalysts may expose less active sites for reaction. Mn did not exhibit FTO activity alone. Although Co and Ni exhibit activity for the FT reaction, the activity of Co and Ni for the FTO reaction is not as high as that of Fe [26]. The Fe-Co catalyst activity was also slightly lower than Fe_3O_4.

The pure Fe_3O_4 catalyst provides 17.3% selectivity of CH_4 and 27.5% selectivity of C_2-C_4 olefins, as well as 16.7% selectivity of CO_2.