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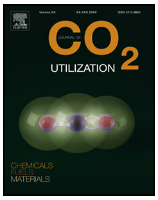

Selective formation of light olefins from CO_2 hydrogenation over Fe–Zn–K catalysts

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ABSTRACT

Fe–Zn–K catalysts were prepared in varied Fe/Zn molar ratios using microwave-aided hydrothermal procedure followed by K modification with impregnation method and applied to CO_2 hydrogenation reaction via Fischer–Tropsch synthesis for the selective production of C_2–C_4 olefins. Results showed that the prepared catalysts had uniform particles within about 100 nm. Addition of zinc to iron matrix formed $ZnFe_2O_4$ spinel phase and ZnO phase, and caused increase of the surface areas, enhanced the interaction between iron and zinc and altered the reduction and CO_2 adsorption behaviors. The catalysts displayed high activity for the CO_2 conversion and significant improvement in the product distribution. The proper interactions between Fe and Zn proved to be advantageous to suppress the production of C_5^+ hydrocarbons and promote the production of C_2–C_4 olefin. At set reaction conditions of H_2/CO_2 of 3, GHSV of 1000 h^{-1}, 320 °C, and 0.5 MPa, the 1Fe–1Zn–K catalyst with H_2/CO reduction showed the best performance with the CO_2 conversion of 51.03%. The selectivity of C_2–C_4 olefins in overall hydrocarbons and the ratio of olefin to paraffin in the C_2–C_4 fraction reached 53.58% and 6.86, respectively.

1. Introduction

The utilization of CO_2 as carbon feedstock to obtain highly added-value chemicals is of importance [1,2]. Among various transformation routes, the chemical conversion of CO_2 via hydrogenation has been considered as one of the most promising processes to produce chemicals such as methanol, higher alcohols and light olefins over modified Fischer–Tropsch synthesis (FTS) [1–5]. Direct synthesis of lower olefins from CO_2 hydrogenation is desired from the viewpoint of converting CO_2 to the building-block chemicals and has progressed in recent years [3,4]. To raise the selectivity toward light olefin products, more effective catalysts need to be discovered considering the thermodynamic inertness of CO_2 and the poor product distribution via FTS.

Traditional FTS catalysts such as iron-based catalysts has been used in CO_2 hydrogenation [1–7] due to high activity for both the water gas shift (WGS) and the reverse water-gas shift (RWGS) reactions during F–T synthesis [4,8,9]. CO_2 hydrogenation on iron catalysts has manifested to proceed via a two-step process with initial conversion of CO_2 to CO via the RWGS reaction followed by the conversion of CO to hydrocarbons via F–T synthesis [4,8]. Iron catalysts are employed in the hydrocarbon synthesis because of high selectivity toward the formation of primary olefins [4]. And CO_2 hydrogenation over iron catalysts can produce more light hydrocarbons compared with CO hydrogenation [6]. Therefore, iron based catalysts have been paid much attention in CO_2 hydrogenation [8]. Preparation methods and promoter addition show impacts on the catalytic activity. It is well recognized that potassium addition in iron catalysts enhances the production of olefinic hydrocarbons in CO hydrogenation [6,10,11]. This alkali promotion is also indispensable to raise light olefin selectivity in CO_2 hydrogenation and has been discussed in detail [3,7,12]. Potassium modified Fe/ZrO_2 catalysts prepared by impregnation method was reported for CO_2 hydrogenation with 42% of CO_2 conversion and 46% fraction of C_2–C_4 olefins in all hydrocarbon products [3]. Further, activity improvement for CO_2 hydrogenation necessitates promoter addition in iron catalysts to enhance the CO_2 adsorption while reduce the secondary hydrogenation ability and suppress heavy products. Manganese and copper, which function as both structural and electronic promoters of modified iron catalysts for CO_2 hydrogenation, have been studied and showed improved activity and selectivity toward light olefins [13,14]. Moreover, it is noteworthy that zinc promoter has been demonstrated to accelerate the FTS reaction and increase stability of the catalysts [15], to enhance the light olefin selectivity and improve CO_2 adsorption [15,16], to promote the hydrogen

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dissociation [17] and be highly active in both the WGS and the RWGS reactions [18,19]. Although the promotion effect of zinc on FTS and methanol synthesis catalysts have been examined [15], the effect on the catalytic hydrogenation of CO_2 to hydrocarbons has not been addressed well.

In this work, a series of potassium promoted Fe–Zn catalysts with varied Fe/Zn molar ratios were prepared by microwave-aided hydrothermal procedure followed by incipient wetness impregnation. The catalysts exhibited excellent activity for CO_2 hydrogenation and high selectivity toward C_2–C_4 olefins owing to the promotion effects of zinc on iron catalysts. The relationship between the structure and the surface properties of the catalysts was discussed by means of characterization of physicochemical properties.

2. Experimental

2.1. Catalyst preparation

Fe–Zn catalysts were prepared using $Fe(NO_3)_3·9H_2O$, $Zn(NO_3)_2·6H_2O$ as Fe, Zn sources, respectively, and urea as precipitator. The Fe/Zn molar ratios for series of preparation samples were 3:1, 1:1, 1:3 and 1:5 and the (Fe + Zn)/urea molar ratio was 1:2 for all the samples. First, desired amounts of $Fe(NO_3)_3·9H_2O$, $Zn(NO_3)_2·6H_2O$ and urea were dissolved and mixed in desired amount of deionized water. Then, the mixed solution was put into a 100 mL Teflon-lined stainless steel autoclave, being kept at microwave conditions of 2450 MHz, 400 W and 1.6 MPa for 90 min. The pH value of the final mixture was about 11. Next, the products were filtered, washed, dried at 120 °C overnight and calcined in the air at 450 °C for 4 h. The obtained powder samples were further impregnated with the aqueous solution of potassium carbonate in the Fe/K molar ratio of 10:1, and dried at 120 °C for 8 h. Finally, all the catalyst samples were pressed into pellets (20 MPa), crushed and sieved to obtain 20–40 mesh for characterization and activity test. The obtained catalyst samples were named as Fe_2O_3–K, 3Fe–1Zn–K, 1Fe–1Zn–K, 1Fe–3Zn–K and 1Fe–5Zn–K, respectively. For performance comparison, other samples labeled as 1Fe–1Mn–K, Fe_2O_3 and ZnO without K promotion were prepared following the same procedure as mentioned above.

2.2. Catalyst characterization

The BET surface areas of the fresh catalysts were measured at −196 °C in a JW-BK132F type N_2 physisorption equipment. 200 mg sample was degassed under vacuum at 300 °C for 2 h prior to measurement. The surface area was determined using the Brunauer–Emmett–Teller (BET) equation based on single point method.

The microscopic morphology was observed on a JEOL JSM-6360LV scanning electron microscope (SEM) equipped with a JED-2300 energy dispersive spectroscopy (EDS) surface element analysis system. Sample was prepared using a JEOL JFC-1600 Auto Fine Coater.

Powder XRD measurements for all the fresh and spent catalysts were performed on a Rigaku D/MAX-2200PC X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å), 40 kV, 30 mA at scanning speed of 8°/min from 5° (2θ) to 85°.

H_2 temperature-programmed reduction (H_2-TPR) measurement of the fresh catalysts was carried out on a TP-5000 chemisorption analyzer. Sample of 50 mg was pretreated with He (mL/min) at 350 °C for 1 h, and then cooled to room temperature. The sample was reduced by a reducing gas (25 mL/min) composed of 5% H_2/95% N_2 as the sample was heated from room temperature to 800 °C at a rate of 10 °C/min.

Temperature-programmed desorption (CO_2-TPD) measurement was performed in the same TP-5000 chemisorption analyzer. 200 mg sample was loaded in the reaction tube and was pretreated with H_2/CO (2:1) (30 mL/min) at 300 °C for 4 h, and then purged with He (50 mL/min) at 300 °C for 30 min prior to measurement. Then the sample was adsorbed with CO_2 at 50 °C until saturation, following by purge with He (mL/min) for 30 min. In all the cases, the TPD measurement was performed from room temperature to 700 °C at a heating rate of 10 °C/min.

The X-ray photoelectron spectra (XPS) was recorded on a thermo scientific ESCALAB 250 spectrometer using an Al Kα X-ray source, where the base pressure of the chamber was less than 2×10^{-8} Pa. The binding energies (BEs) were calibrated relative to adventitious carbon using the C 1s peak at 284.8 eV.

2.3. Catalytic activity tests

The CO_2 hydrogenation reaction over prepared Fe–Zn–K catalysts was performed in a stainless flow-type pressurized fixed-bed reactor (8 mm i.d., 400 mm in length) with 2 mL of catalyst. The ratio of height to diameter (H/D) of the catalyst bed was about 5. All the samples were pre-reduced by syngas with H_2/CO of 2 at 1000 h^{-1}, 0.5 MPa and 300 °C for 4 h. H_2 and H_2/CO_2 pretreated 1Fe–1Zn–K sample was also conducted at 1000 h^{-1}, 0.5 MPa and 300 °C for 4 h for comparison. The typical reaction conditions were as follows: $H_2/CO_2 = 3$ (molar ratio), GHSV = 1000 h^{-1}, p = 0.5 MPa and T = 320 °C. The effluent gas was analyzed on an online gas chromatograph (GC-9560-I), with a 2 m TDX-01 packed column for C_1 products analysis via TCD detector, and a 50 m Al_2O_3 capillary column for C_1–C_5 hydrocarbons products via FID detector, respectively. The liquid products were analyzed on an off-line gas chromatograph (GC-9560-II), with a 2 m GDX-401 packed column for the aqueous phase products analysis via TCD detector and a 30 m SE-30 capillary column for the oil phase products analysis via FID detector. The mass balance was based on carbon and the results were calculated in terms of activity by CO_2 conversion, light olefin selectivity (wt.) by olefin fraction in overall hydrocarbon products and olefin to paraffin ratio (O/P) in the C_2–C_4 fraction.

3. Results and discussion

3.1. Phase structure of the catalysts

The XRD patterns of the fresh catalyst samples are shown in Fig. 1. The diffraction peaks assigned to rhombohedral hematite (α-Fe_2O_3) [15] were observed for the Fe_2O_3 sample (Fig. 1a) and K promoted Fe_2O_3 sample (Fig. 1b). As the zinc content increased (Fig. 1c–f), the diffraction peaks at 2θ = 30.5°, 35.4°, 36.9°, 43.1°,

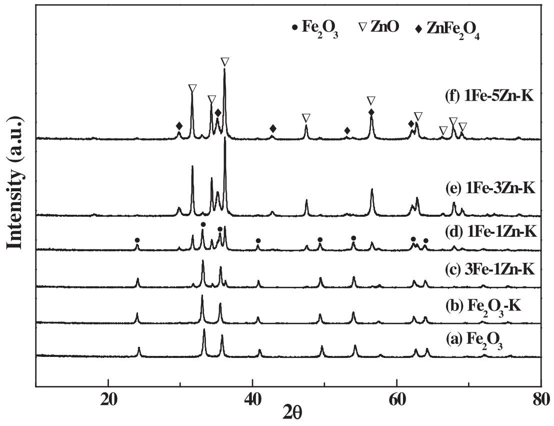

Fig. 1. XRD patterns of fresh catalyst samples.