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Article

Effects of zinc on Fe-based catalysts during the synthesis of light olefins from the Fischer-Tropsch process

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ABSTRACT

Fe-based catalysts for the production of light olefins via the Fischer-Tropsch synthesis were modified by adding a Zn promoter using both microwave-hydrothermal and impregnation methods. The physicochemical properties of the resulting catalysts were determined by scanning electron microscopy, the Brunauer-Emmett-Teller method, X-ray diffraction, H_2 temperature-programed reduction and X-ray photoelectron spectroscopy. The results demonstrate that the addition of a Zn promoter improves both the light olefin selectivity over the catalyst and the catalyst stability. The catalysts prepared via the impregnation method, which contain greater quantities of surface ZnO, exhibit severe carbon deposition following activity trials. In contrast, those materials synthesized using the microwave-hydrothermal approach show improved dispersion of Zn and Fe phases and decreased carbon deposition, and so exhibit better CO conversion and stability.

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1. Introduction

Light olefins (C_2 to C_4) are widely used in the synthesis of plastics, drugs, solvents and cosmetics. In conventional industrial processes, light olefin products are produced through the catalytic cracking of crude oil feedstocks [1,2]. However, because of the growing global demand for bulk chemicals and the ongoing depletion of petroleum reserves, the industrial production of light olefins is threatened by both environmental and economic factors. Recently, the synthesis of light olefins from syngas (CO/H_2) has received significant attention because this approach derives olefins from nonpetroleum carbon resources such as coal, natural gas and biomass [1–3]. In general, two or more stages are required for such syntheses, including the cracking of Fischer-Tropsch (FT)-derived heavy hydrocarbons and the dehydration of FT-derived methanol to light olefins [2,4]. Compared with these multistage reaction processes, a Fischer-Tropsch olefins (FTO) synthesis directly from syngas without intermediate steps would be more energy efficient and economical [1,4].

Fe-based catalysts allow the selective formation of light olefins from CO hydrogenation in reactions that are less expensive and that show low methane and high olefin selectivity, compared with the results obtained from catalysts based on Co, Ru and other metals [1,5–7]. In the case of Fe-based catalysts, there has been much research focused on the optimization of

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support substances such as α-Al_2O_3, SiO_2 or carbon materials [2,4]. However, compared with these supported catalysts, the use of low cost, unsupported bulk catalysts showing competitive olefin selectivity is still of interest [1]. In addition to the development of supported and unsupported catalysts, many groups have focused on examining possible catalytic promoters. Recently, de Jong's group [2] reported that the addition of Na and S produces Fe-based catalysts with high selectivity for light olefins, while Qiao's group [8] showed that K can act as a promoter when used with iron supported on graphene, and enhances the light olefin selectivity. Furthermore, transition metals such as Mn, Zr, V and Cr on Fe-based catalysts are also effective promoters [7–14]. Despite this prior work, there has been little research regarding the selectivity for CO_2 during the promotion of the FTO reaction over Fe-based catalysts.

Our previous work [15] has shown that Fe-Zr catalysts prepared by a microwave-hydrothermal method improve the catalytic activity during CO conversion and also decrease the selectivity for CO_2. However, these catalysts generate a broad spectrum of products, and so it is necessary to further increase their selectivity for light olefins in the C_2 to C_4 range. A Zn promoter has previously been reported [10,12] to increase FTO reaction rates and to enhance the light olefin selectivity over an iron catalyst, although the possibility of severe carbon deposition has been neglected when examining such Zn-promoted catalysts [13,14].

In the present work, we propose a new strategy with regard to the use of Zn promoters to enhance light olefin selectivity and to decrease carbon deposition on Fe-based catalysts. Herein, the effects of a Zn promoter on the structure and catalytic performance of such catalysts is discussed, with the aim of elucidating the function of the Zn promoter.

2. Experimental

2.1. Catalyst preparation

Fe-Zr precursors with an Fe/Zr atomic ratio of 6 were prepared using a microwave-hydrothermal method, as reported previously [15]. In a typical reaction, both $Fe(NO_3)_3{\cdot}9H_2O$ (Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China) and $ZrO(NO_3)_2{\cdot}2H_2O$ (Tianjin Guangfu Fine Chemical Research Institute) were added to a Teflon tube containing an aqueous urea (Tianjin Guangfu Fine Chemical Research Institute) solution, at an (Fe+Zr)/urea molar ratio of 0.5. This mixture was subsequently subjected to microwave-hydrothermal treatment at 2450 MHz and 1.6 MPa over 2 h. The resulting solid product was filtered, washed with deionized water, dried at 120 °C for 12 h and finally calcined at 500 °C for 3 h to obtain the Fe-Zr precursor.

Fe-based catalysts with different ZnO contents were obtained by impregnating the above Fe-Zr precursors with an aqueous solution of $Zn(NO_3)_2{\cdot}6H_2O$ (Tianjin Guangfu Fine Chemical Research Institute). Following this impregnation, the solid samples were dried at 80 °C for 8 h and then calcined at 350 °C for 3 h. Subsequently, 2 wt% K_2CO_3 (Tianjin Guangfu Fine Chemical Research Institute) was added to each solid sample using incipient wetness impregnation. After drying overnight at 120 °C, catalysts were obtained having specific ZnO contents of 0, 10, 20 and 40 wt%, denoted as Zn0, Zn10, Zn20 and Zn40, respectively.

To compare the impregnation of 20 wt% ZnO on Fe-based catalysts, we also employed $Fe(NO_3)_3{\cdot}9H_2O$, $ZrO(NO_3)_2{\cdot}2H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ in a one-step microwave-hydrothermal process to prepare an Fe-Zr precursor containing a Zn promoter. In this trial, 2 wt% K_2CO_3 was also employed in the same manner to improve the catalytic performance. This catalyst is denoted as Zn20[M]. All the above catalyst samples were crushed and sieved to obtain particles of sizes 20–40 mesh prior to characterization and activity tests.

2.2. Catalyst characterization

The Brunauer-Emmett-Teller (BET) surface areas of the fresh catalysts were measured at −196 °C using a JW-BK132F N_2 physisorption instrument (Beijing JWGB Sci. & Tech. Co., Ltd.). In these trials, 200-mg samples were held under vacuum at 300 °C for 2 h prior to each measurement. The surface areas were determined using the BET equation based on the single point method. The microscopic morphologies of specimens were obtained by scanning electron microscopy (SEM) with a KYKY-2800B instrument at an accelerating voltage of 25 kV. Powder X-ray diffraction (XRD) patterns of both fresh and used catalysts were acquired with a Rigaku D/MAX-2200PC X-ray diffractometer with Cu K_α radiation (λ = 0.15406 nm) at 40 kV and 30 mA and at a scan rate of 8°/min from 5° to 85° (2θ). H_2 temperature-programmed reduction (H_2-TPR) measurements of fresh catalysts were carried out on a TP-5000 analyzer equipped with a quartz tube reactor. In these measurements, 50-mg catalyst samples were calcined at 500 °C and then pretreated with He (30 mL/min) at 350 °C for 1 h, after which they were cooled to room temperature. Each sample was exposed to a 5% H_2-95% N_2 mixture at a flow rate of 30 mL/min with heating from room temperature to 890 °C at a rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) data were obtained for both fresh and used samples with a Thermo Scientific ESCALAB 250 spectrometer using an Al K_α X-ray source, with the base pressure of the chamber below 20 nPa. The binding energy (BE) was calibrated relative to that of adventitious carbon, using the C 1*s* peak at 284.8 eV.

2.3. Catalytic reaction

The FTO reaction was carried out in a micro-type fixed-bed reactor system (i.d. = 8 mm; length = 400 mm) with 2 mL catalyst samples. Prior to each reaction, each catalyst sample was pretreated in the syngas flow (H_2/CO = 2) at 1000 h^{-1}, 280 °C and 0.1 MPa for 4 h. The temperature was subsequently increased to 340 °C and pressure was raised to 1.5 MPa to start the reaction. The products were analyzed with an on-line gas chromatograph (GC-9560-I), using a 2-m TDX-01 packed column for C_1 products analysis and a 50-m Al_2O_3 capillary column for C_1–C_5 hydrocarbons products. The liquid products were analyzed on an off-line gas chromatograph (GC-9560-II), with a

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