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Synthesis of light olefins from CO hydrogenation over Fe–Mn catalysts: Effect of carburization pretreatment

Jian-li Zhang [a,*], Li-hai Ma [a], Su-bing Fan [a], Tian-Sheng Zhao [a,*], Yu-han Sun [b]

[a] State Key Laboratory Cultivation Base of Natural Gas Conversion, Ningxia University, Yinchuan 750021, China
[b] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, China

HIGHLIGHTS

- Carburizaiton pretreatment promoted CO adsorption on Fe–Mn–K catalysts.
- The catalysts with CO and syngas pretreatment showed much higher selectivity to light olefin than that pretreated with H_2.
- Formation of carbide species improved the surface basicity.
- The improved surface basicity reduced the second hydrogenation reaction.

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ABSTRACT

Effects of carburization during pretreatment with different atmospheres on K promoted Fe–Mn catalysts for CO hydrogenation were investigated. The bulk structure, surface composition and chemical properties of the catalysts before and after pretreatment were characterized by means of X-ray diffraction (XRD), Raman spectroscopy, in situ X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption/oxidation (TPD/TPO) and catalytic activity tests for the selective formation of light olefins. Results indicated that the surface basic sites and CO adsorption were promoted after pretreatment, especially for CO pretreatment. As the formation of iron carbide and elevation of carburization temperature, the surface basicity was significantly enhanced. The catalysts after CO or syngas pretreatment exhibited much higher selectivity to light olefin than that pretreated with H_2 due to the basicity change during the pretreatment. The formation of carbide species improved the surface basicity which enhanced the adsorption and dissociation of CO and then decreased the second hydrogenation of primary olefins.

1. Introduction

The conversion of syngas to light olefins (STO) via Fischer–Tropsch synthesis has been considered as a possible solution to meet the growing demands for chemical feedstocks such as ethylene, propylene and butylene. Modified iron catalysts have shown the great prospects for selective formation of light olefins from CO hydrogenation [1–7], which produce more olefin while lower CH_4 products than other catalysts over a wide range of reaction temperature and H_2/CO ratio [8–12]. Nevertheless, secondary reactions as hydrogenation and polymerization by the readsorption of primarily formed olefin [10] bring disadvantage effect on the formation of light olefin in addition to the limitation by Anderson–Schulz–Flory (A–S–F).

Researches indicated that activation of iron catalyst in different atmospheres produced significant effects on its performance [13–20]. Soled et al. [21] suggested that catalysts with main iron oxides rather than iron carbide conducted secondary hydrogenation and showed lower olefin selectivity. Pretreatment with CO was more effective than other pretreatment [14,15,17,20] and promoted the olefin selectivity [14,15,20]. Bukur et al. [14,22] reported that the partially carbided surface by CO pretreatment inhibited the second reactions and thus the olefin selectivity was the highest over the CO reduced catalyst. The catalytic behaviors of heterogeneous catalysts are mainly determined by their surface properties [4]. The formation of carbide species on iron catalysts during either the carburization pretreatment or the reaction process has significant effect on the surface chemical nature and catalytic performance although the controversy still remains on the role of iron carbides during Fischer–Tropsch synthesis [23–25].

In order to further explore the reason responsible for improved light olefin selectivity after carburization pretreatment, the effects of carburization on the olefin selectivity due to the change of

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* Corresponding authors. Tel./fax: +86 951 2062323.
E-mail addresses: zhangjl@nxu.edu.cn (J.-l. Zhang), zhaots@nxu.edu.cn (T.-S. Zhao).

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surface composition and chemical nature of iron–manganese catalysts were investigated in this study.

2. Experimental

2.1. Catalyst preparation

The catalyst precursor was prepared by coprecipitation from a mixed aqueous solution of iron and manganese nitrates in a desired Fe/Mn molar ratio of 3/1 using ammonia as precipitator. The precipitate was washed with deionized water, filtered and dried at 353 K for 48 h, following calcination in air at 723 K for 90 min according to a controlled decomposition method [26]. Then the obtained sample was impregnated with an aqueous solution of potassium carbonate (2 wt.%) by incipient wetness method and dried at 353 K for 24 h. The carburization pretreatment was conducted as follows: oxide precursor (mg) was loaded in a quartz tube placed in an electronically heated furnace and contacted with pure CO in a flow rate of 1000 h^{-1} at atmospheric pressure at 523 K, 573 K and 673 K, respectively, for 4 h. Then the sample was cooled down to room temperature and passivated in a 1 vol.% O_2 in N_2 stream. Finally the sample was crushed and pulverized to 40–60 mesh. Other two samples for comparison were pretreated by pure H_2 and syngas (H_2/CO = 2/1) at 573 K for 8 h and 553 K for 8 h, respectively, following the same procedure as CO pretreatment.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns of the catalyst samples were measured on a Rigaku D/Max 2500 powder diffractometer using Cu Kα radiation operated at 40 kV and 40 mA.

Raman spectra of the pretreated samples after passivation in N_2/O_2 (1 v%O_2) were collected on a Renishaw-Uv–Vis Raman System 1000 (Kaiser Optical) using a frequency-doubled He:Cd laser at a wavelength of 325 nm. The Raman spectrometer was equipped with a CCD camera that was electrically cooled to 233 K in order to reduce thermal noise. Rotating-sample techniques were used to prevent the decomposition and/or reduction by the laser beam. A total of 50 mg of a powdered sample were mounted on a treatment chamber.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG MiltiLab 2000 spectrometer, and all spectra were obtained using Mg Kα X-ray source. All XPS spectra were obtained from the samples treated in situ in the reaction cell and then transferred into the ultra high vacuum (UHV) chamber without exposure to air. Binding energies (BEs) were calibrated relative to the C 1s peak from carbon contamination of the samples at 284.6 eV to correct for the contact potential differences between the sample and the spectrometer.

Temperature-programmed desorption (CO_2-TPD and CO-TPD) measurements were performed in a flow reactor on TPD-MS equipment and the effluent gas was detected by a Balzers Omnistar QMS200 quadrupole mass spectrograph. The samples after different pretreatment were cooled to room temperature and flushed with Ar for 1 h prior to TPD measurement, and then treated with CO_2 and CO respectively at room temperature until saturation, following flushing with Ar for 1 h. In all the cases, the TPD measurement was performed from room temperature to 1173 K at a heating rate of 10 K/min.

Temperature-programmed oxidation (TPO) was used to detect different carbon species after pretreatment in a quartz reactor equipped with MS to detect the composition of the effluent gas. The catalyst samples after different pretreatment were cooled to room temperature and flushed with Ar for 1 h prior to TPO measurement. The gas consisted of 5 v% O_2 in Ar at a flow rate of 50 mL/min and the profiles were recorded by heating the samples from 323 K to 1073 K at a linear heating rate of 10 K/min. In all the cases, the weight of the sample used was 50 mg.

2.3. Catalyst tests and product analysis

The catalytic activity tests of the catalyst samples were performed in a pressurized integral fixed bed flow reactor in the following conditions: catalyst, 2 mL, H_2/CO = 2:1 (molar feed ratio), GHSV = 1000 h^{-1}, total pressure = 1.5 MPa, T = 593 K.

The feed gas and the products were all analyzed using gas chromatograph. The results were presented in terms of activity by CO conversion (Xco), light olefin selectivity by olefin to paraffin ratio (O/P) in the C_2–C_4 fraction. CH_4 and CO_2 selectivity by molar percentage of CO converted to CH_4 and CO_2 in total CO converted, and the hydrocarbon distribution was expressed as the weight percentage of desired components in all hydrocarbons. The material balance was based on carbon.

3. Results and discussion

3.1. XRD analysis of the catalysts

The XRD patterns of the catalyst samples are shown in Fig. 1. For the sample without pretreatment (Fig. 1a), only weak diffraction peak intensity attributable to α-Fe_2O_3 phase was found and the sample should be highly dispersed. For the CO pretreated sample at 573 K (Fig. 1d) and at 673 K (Fig. 1e), the diffraction peaks of iron carbide were found, being identified mainly as Fe_5C_2 and Fe_3C respectively. However, iron carbide species were hard to distinguish from the XRD patterns for the samples pretreated with CO at 523 K (Fig. 1b) and syngas at 553 K (Fig. 1c) although low amount of carbidic carbon was detected by XPS measurement (see Table 1), which might be concerned with less stable iron carbide as ε'-$Fe_{2.2}C$. For H_2 pretreated sample (Fig. 1f), only small amount of α-Fe was found and most of iron species were stabilized as Fe_3O_4 or in the form of iron–manganese spinel phase [27]. Iron–manganese spinel phase was detected in all the pretreated samples. For the used sample by syngas pretreatment, Fe_3O_4 could be identified (Fig. 1g), however, the diffraction intensity of iron–manganese spinel phase was remarkably weakened after reaction. The used sample was flushed with nitrogen and then passivated in a 1 vol.% O_2 in N_2 stream before it was removed from the reactor,

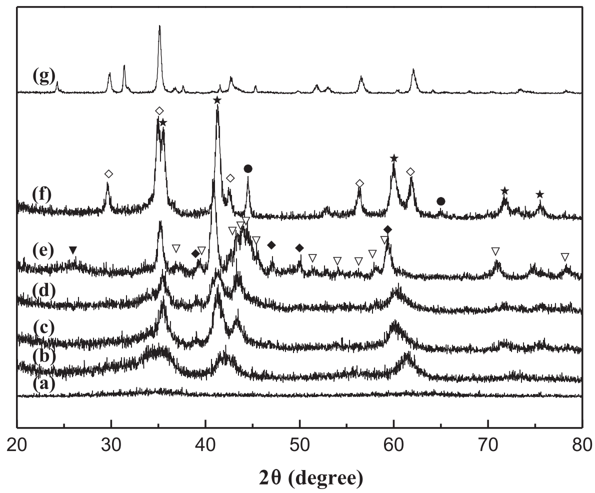

Fig. 1. XRD patterns of the catalysts: (a) as prepared; (b) CO-523K-4h; (c) syngas-553K-8h; (d) CO-573K-4h; (e) CO-673K-4h; (f) H_2-573K-8h; (g) after reaction. ★, FeO–MnO spinel; ◇, Fe_3O_4; ♦, Fe_5C_2; ▽, Fe_3C; ▼, C (graphite); ●, α-Fe.