



Effect of interaction between potassium and structural promoters on Fischer–Tropsch performance in iron-based catalysts

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ABSTRACT

The Fischer–Tropsch synthesis (FTS) performances of iron-based catalysts promoted with/without potassium compounds containing different acidic structural promoters (Al_2O_3 , SiO_2 , and ZSM-5) were studied in this research. Characterization technologies of temperature-programmed reduction with CO (CO-TPR), powder X-ray diffraction (XRD) and Mössbauer effect spectroscopy (MES) were used to study the effect of K–structural promoter interactions on the carburization behaviors of catalysts. It showed that the addition states of potassium (K– Al_2O_3 , K– SiO_2 , K–ZSM-5 and K-free) have a significant influence on the formation of iron carbides, which shows a following sequence in promotion of carburization: K– Al_2O_3 > K– SiO_2 > K–ZSM-5 > K-free. The FTS reaction test was performed in a fixed bed reactor. It is found that Fe/K– Al_2O_3 catalyst leads to the highest CO conversion, Fe/K–ZSM-5 catalyst shows the highest H_2 conversion, and Fe/K-free catalyst shows the lowest CO and H_2 conversion. As for the hydrocarbon selectivity, Fe/K– SiO_2 catalyst yields the lowest methane and the highest C_5^+ products, Fe/K–ZSM-5 catalyst yields higher methane and the highest liquid hydrocarbon product, whereas Fe/K-free catalyst yields the highest methane and the lowest C_5^+ products. These results can be explained from the interaction between potassium and structure promoters, and the spillover of reactants or intermediates from Fe sites to the surfaces of structural promoters.

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1. Introduction

Fischer–Tropsch synthesis (FTS) has been recognized as an important technology in the production of liquid fuels and chemicals from syngas derived from coal, natural gas, and other carbon-containing materials [1]. With the emergency of transportation fuel shortage in the whole world and the pollution from the combustion of fuels refined from petroleum, FTS is becoming a much concerned academic or industrial topic for more and more people, especially in China [2]. The current focus on the FTS process deals with the production of transportation fuels such as gasoline and diesel [3], which can be maximized via oligomerization or hydrocracking of FTS effective hydrocarbons (ethene, propylene or wax). However, traditional FTS iron-based catalysts produce a large amount of methane and gaseous alkanes, which are useless for the utilization of coal or natural gas resources. Therefore, it is expected that more effective hydrocarbons are produced via selectivity control, addition of promoters or some other feasible ways.

It is well known that the promotion of potassium has significant effect on the FTS performance of catalysts [4–7]. That is,

potassium suppresses the production of methane and improves the effective hydrocarbon selectivity. Dry and Oosthuizen [8] studied the correlation between catalysts surface basicity and hydrocarbon selectivity, and found that the surface basicity can apparently suppress the methane selectivity. Alkali potassium can bring high surface basicity to the catalysts, but the acidic sites of structural promoter suppress surface basicity. Bukur et al. [9] studied the effect of potassium on the silica-supported iron catalysts and found that silica can suppress the basicity of the K promoter. Dlamini et al. [10] studied the effect of adding SiO_2 to a precipitated-iron catalyst using scanning electron microscopy analyses and found that the amount of effective K_2O associated with Fe is less when SiO_2 added as a binder. In Yong et al.'s study [11], a potassium-containing catalyst without SiO_2 addition possesses a markedly higher activity than the catalysts containing SiO_2 . The decreased activity with addition of SiO_2 was attributed by authors to the decrease of the effective potassium due to the interaction between potassium and silica. More recently, Zhang et al. [1] observed a much more complex interaction between metal components (Fe, Cu, K) and SiO_2 , which had an apparent effect on the surface properties and FTS performance of catalysts. Similarly, this kind of interaction between potassium and structural promoters was observed in other supported catalysts. For example, an interaction between potassium and alumina exists in alumina-supported cata-

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lysts. Many researchers postulated that the interaction is in a phase of KAlO_2 , and Kotarba [12] studied the role of KAlO_2 phase and the chemical state of potassium in iron catalysts using model compounds (KAlO_2 and KFeO_2) and found that potassium at the surface of catalyst is ionic on KAlO_2 and covalent on KFeO_2 . Jun et al. [13] investigated three iron catalysts with different supports (without support, alumina-supported and silica-supported) for FTS reaction. Their results indicated that Al_2O_3 can dilute and SiO_2 can severely dilute the potassium promotion using temperature-programmed decarburation, whereas Al_2O_3 can help the dispersion of K on Fe-alumina catalyst and SiO_2 makes the K and Fe dispersion worse. Ma et al. [14] studied potassium effects on activated-carbon-supported iron catalysts and this report also indicates that the AC-supported iron catalysts need more of potassium promoter to increase catalyst activity relative to the precipitated-iron catalyst due to the dispersion effect of AC support.

A lot of literature had proved that an interaction between potassium and structural promoters exists in iron-based FTS catalysts. However, little work was conducted to purposefully study the effect of this interaction on the FTS performance. The present work focuses on the interaction between potassium and some structural promoters, and its effect on FTS performances (carburization behavior, activity, stability, and selectivity) of an iron-based catalyst. The structural promoters (SiO_2 , Al_2O_3 , and ZSM-5) with different intrinsic acidities were used to counteract the surface basicity of potassium promoter and to provide different K–structural promoter interactions.

2. Experimental

2.1. Catalysts preparation

The FeMn– SiO_2 precursor used in present study was prepared by a combination method of continuous co-precipitation and spray-drying technology, detailed making method is described in literature [1]. Then potassium promoter with Fe/K mole ratio of 100/3 was added to the precursor using the method of mechanically mixed with the different compounds of potassium: K–ZSM-5, K– SiO_2 and K– Al_2O_3 . These catalysts were signed as Fe/K-free, Fe/K–ZSM-5, Fe/K– SiO_2 , and Fe/K– Al_2O_3 separately, and the detailed description of catalysts is presented in Table 1.

2.2. Reactor system and operation procedure

The experiments were conducted in a 12 mm i.d. stainless steel fixed bed reactor with an effective bed length of approximately 15 cm (15 cm^3 bed volume). For all the experiments, approximately 3 g catalysts (20–40 mesh) were filled in the reactor, the remaining volume of reactor was filled with quartz granules with the diameter of 10–20 and 20–40 mesh. All the catalysts were reduced with

Table 1
Description of catalysts

Catalyst no.	Description
Fe/K-free	FeMn– SiO_2 blank sample was dried at 120°C overnight and calcined at 500°C for 5 h.
Fe/K–ZSM-5	Promoted with K–ZSM-5. K–ZSM-5 was prepared via ion-exchanging of H–ZSM-5 with a KOH solution, dried at 120°C overnight and calcined at 500°C for 5 h.
Fe/K– SiO_2	Promoted with K– SiO_2 . K– SiO_2 was prepared from drying of potassium water glass at 120°C overnight and calcined it at 500°C for 5 h.
Fe/K– Al_2O_3	Promoted with K– Al_2O_3 . K– Al_2O_3 was prepared with mixing a KOH solution with aluminous sol, dried at 120°C overnight and calcined at 500°C for 5 h.

syngas ($\text{H}_2/\text{CO} = 2.0$) at 280°C , 0.5 MPa, and 1000 h^{-1} for 16 h, then the reactor was cooled down to 160°C . Then the pressure of the system was set to 1.50 MPa, and the temperature was gradually increased to 250°C by $10^\circ\text{C}/\text{h}$. The time on steam of all catalysts is about 120 h. The product in the hot and cold traps were collected over 24 h, weighted and sampled for analysis. During every mass balance period, the tail gas was analyzed twice.

2.3. Catalysts characterization

Temperature-programmed reduction (TPR) was used to measure the rate of carburization of different K-promoted catalysts. Catalysts (80 mg) were loaded into a quartz tube reactor and first heated to 500°C and kept for 30 min, and then cooled to ambient temperature in Helium gas. The flow was then switched to 5%CO/95%He and the reaction temperature was increased to 1000°C at rate of $10^\circ\text{C}/\text{min}$. The consumption of reactant gas was monitored by mass spectroscopy.

Powder X-ray diffraction (XRD) measurements were carried out using a D-5000 Siemens diffractometer and Cu $\text{K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$).

The Mössbauer effect spectroscopy (MES) was used to test the structure of the catalysts after reduction and reaction, which measured with a CANBERRA Series 40 MCA constant-acceleration Mössbauer spectrometer (CANBERRA, USA) at room temperature, using a 25 m Ci ^{57}Co in Pd matrix.

3. Results

3.1. CO-TPR

Fig. 1 is CO-TPR profiles of all catalysts. It can be seen that Fe/K-free, Fe/K–ZSM-5 and Fe/K– Al_2O_3 catalysts all have three reduction/carburization peaks and Fe/K– SiO_2 catalyst has two peaks in the temperature range of $200\text{--}300^\circ\text{C}$ which is ascribed to the reduction of Fe_2O_3 to Fe_3O_4 . The second peak located in $400\text{--}550^\circ\text{C}$ is corresponding to the carburization of iron oxides, and the peak after 600°C is corresponding to the carburization of the difficultly reduced iron oxide phase. The addition of potassium has a marked effect on these carburization peaks. That is, all states of potassium promoters move the reduction/carburization peaks to lower temperature and strengthen the peak intensity in different extents. Specifically, the addition of K–ZSM-5 is less promotional on the carburization, which only

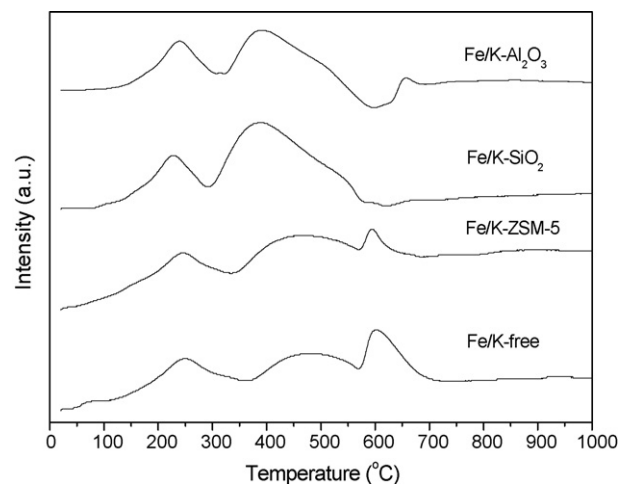


Fig. 1. CO-TPR profiles of all four catalysts.

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