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Factors influencing the Fischer–Tropsch synthesis performance of iron-based catalyst: Iron oxide dispersion, distribution and reducibility

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ABSTRACT

The performances of iron-based catalysts supported on SiO_2, TiO_2 and TS-1 for the Fischer–Tropsch synthesis (FTS) were investigated in a fixed-bed reactor. The results showed that Fe/TS-1 catalyst exhibited better FTS performance than Fe/TiO_2 and Fe/SiO_2 with higher CO conversion and C_{5+} selectivity. The desilication treatment of TS-1 further increased the FTS performance of Fe/TS-1 catalyst in terms of activity and stability. These iron-based catalysts were characterized by N_2 adsorption, H_2 temperature-programmed reduction, X-ray diffraction, transmission electron microscopy, scanning electronic microscopy and thermal gravimetric analysis. The factors influencing the FTS performance of the iron-based catalyst were discussed and the results indicated that not only the dispersion but also the reduction degree of iron oxides increased after desilication treatment of TS-1 support through generating more mesoporous structures and increasing the crystallinity degree of TS-1. The improved FTS activity is due to the increased dispersion of iron particles without affecting the original reducibility. The better stability is due to the enhanced heat and mass transfer as well as the high resistance against coke formation and deposition.

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1. Introduction

The severe environmental regulations together with the dwindling nonrenewable energy sources are the main driving force for seeking environmentally alternative energy source and the development of the clean energy. Fischer–Tropsch synthesis (FTS) receives more attention nowadays because it can transform the syngas derived from coal, natural gas or biomass to ultra-clean transportation fuels and bulk chemical feedstock in a non-petroleum route. Even though several metals have demonstrated activity for the FTS reaction, only iron and cobalt catalysts have been used in the industrial application for their high activity and appropriate cost [1,2]. Cobalt catalyst is considered as a good choice especially in the low-temperature FT processes for its high activity, high selectivity to linear paraffins, high resistance toward deactivation and low water–gas-shift activity, etc. [1,3]. Compared to the Co catalyst, the iron-based catalyst also attracted extensive attention not only due to its relatively cheap price but also its high water–gas-shift activity. And thus it can adjust the H_2/CO ratio in H_2-deficient or CO_2-rich syngas to condition the FTS reaction. What is more, the light olefins or oxygenated hydrocarbons with high yield on iron-based catalyst can be well controlled by tuning the reaction parameters. These properties make iron-based catalyst a more attractive candidate for the new generation FTS catalyst than the Co catalyst [4–6].

For the iron-based catalysts, previous work mainly focuses on the precipitated iron catalysts in a view of industry. In recent years, many researchers began to pay attention to the supported iron catalyst. The role of the support is to disperse the active phase, reduce the amount of active component, stabilize the active species and effectively remove the heat generated in such an exothermal reaction. As generally known, the textural properties of the supports have a great influence on the catalytic performances. For this reason, a number of oxides (SiO_2, Al_2O_3, TiO_2, MgO and ZrO_2) have been used to support iron-based catalysts for FTS. However, these oxide supports are prone to being interacted with the Fe species to form Fe intermediates difficult to be reduced, which deteriorates the FTS activity. Since zeolites have been widely used in the petrochemical and refining industry for its special properties such as high surface area, high thermal stability, intrinsic acidity, well-defined microporosity, etc., many efforts have been done to use zeolites as supports for preparing FTS catalysts or others [2,7–13]. Among them, silicatelaluminosilicate molecular sieve with regular, well-defined and tunable channel system is widely applied as the support to prepare iron-based catalyst for FTS. However, the silicatelaluminosilicate molecular sieve supported iron-based catalyst suffered high selectivity for undesired low molecular weight hydrocarbons and high deactivation rates due to the high acidity caused by the aluminum in the framework, which thus restricted its application in the FTS [9,14,15]. The titanium silicalite-1 (TS-1), which shares the same Mobil Five (MFI) structure with silicatelaluminosilicate molecular sieves, can alleviate this problem by substituting Ti for Al. Since its invention in 1983, the TS-1 has been

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Table 1
Structural and textual properties of the supports and the iron catalysts.

Sample	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
SiO_2	535	0.79	4.8
TiO_2	54	0.19	15.1
TS-1	440	0.23	5.0
Fe/SiO_2	367	0.52	4.7
Fe/TiO_2	47	0.17	16.4
Fe/TS-1	321	0.19	9.1

extensively used as support owing to its large specific surface area and rich microporous structure [11,12,16,17]. However, the iron-based catalyst supported on TS-1 for FTS has not yet been studied.

For the iron-based catalysts, high deactivation rate is a main challenge from the viewpoint of economic feasibility. Coke deposition on the catalyst surface is the main reason for the loss of the catalytic activity, especially for the catalyst supported on MFI zeolite. Since TS-1 zeolite has abundant microporous structure, the steric effect and diffusion limitation may restrain its application in FTS reaction due to coke formation and the inhibition of chain growth. As reported, the TS-1 with mesopores has high resistance toward coke deposition due to the enhanced mass transfer of coke precursor [15,18]. So, zeolite with mesoporous structure is considered to be a particularly alternative approach and the well-developed mesoporosity is beneficial for the process of mass transfer of reactant molecules or product molecules, which is helpful for improving the catalytic performance in a series of reactions [19]. For this purpose, a mass of approaches have been developed to improve the proportion of mesopores in zeolite. Among these methods, the post desilication is reported to be a simple, feasible and the most promising approach [11,15,18,20]. And it is important how the desilication procedure is performed. It was reported that the mild alkaline solutions like Na_2CO_3 treated HZSM-5 result in better catalytic performance in the methanol to gasoline reaction than the NaOH treated HZSM-5 [20]. However, only a few reports discussing the catalytic performance of desilicated HZSM-5 have been published and the whole properties of desilicated zeolites have not been investigated. Furthermore, the effect of desilication of TS-1 on the FTS performance of Fe/TS-1 is unclear. It may be helpful to comprehensively study around the desilication of TS-1 zeolite and its application in the FTS reaction.

In this study, TS-1 supported iron catalyst was prepared and compared with SiO_2 and TiO_2 supported iron catalysts for FTS performance. The effect of Na_2CO_3 solution on TS-1 supported Fe catalyst performance in the FTS process was also investigated. Especially the desilication effect of Na_2CO_3 solution on TS-1 was discussed. The catalysts were characterized by a series of techniques to get the factors affecting the FTS performance of the iron-based catalyst.

2. Experimental

2.1. Catalyst preparation

The supports used for iron-based catalysts preparation were purchased from different companies. SiO_2 was supplied by Qingdao Yuminyuan Silica-Gel Reagent Factory of China. TiO_2 was supplied by Tianjin Kermel Co. of China. TS-1 was supplied by Nankai Catalyst Co. of China. All the chemicals were used without any further treatment.

The 20 wt.% iron catalysts supported on the support SiO_2, TiO_2 or TS-1 for FTS were prepared by the incipient wetness impregnation method. After impregnation, the catalyst was dried in an oven for 12 h at 110 °C and then calcined in an air flow at 400 °C for 5 h with a rate of 3 °C/min. Finally, the prepared catalysts were designed as Fe/SiO_2, Fe/TiO_2 and Fe/TS-1, respectively.

The desilication process of TS-1 was as follows based on the report from Fathi et al. [20]: the fresh TS-1 sample was treated with 0.1 M Na_2CO_3 solution (15 mL/g-zeolite) for 3 h at 75 °C followed by washing with deionized water until pH value was close to 7. After drying overnight at 110 °C, the sample was ion exchanged twice with a 1.0 M NH_4NO_3 solution (15 mL/g-zeolite) at 75 °C followed by drying at 110 °C for 12 h and calcination at 500 °C for 3 h to obtain protonated sample. The sample was named as TS-1-D1. For comparison, TS-1 desilicated by Na_2CO_3 for 6 h was prepared and labeled as TS-1-D2. Their corresponding catalysts were prepared by incipient wetness impregnation method with the same procedure as Fe/TS-1, being denoted as Fe/TS-1-D1 and Fe/TS-1-D2 respectively.

2.2. Characterization of the supports and iron catalysts

The textual properties of the supports and the corresponding catalysts were determined by the N_2 adsorption–desorption performed at −196 °C in Micromeritics Tristar-3000 analyzer. Each sample was degassed at 90 °C for 1 h and 300 °C for 4 h to remove the moisture adsorbed at surface and internal pores prior to the measurement.

The powder X-ray diffraction (XRD) characterization was performed on a RigakuD/max-2500 diffractometer with a CuKα radiation (40 kV, 200 mA). The scan speed was 8°/min, with a scanning angle ranged from 5° to 85°. The average size of the α-Fe_2O_3 crystallites was estimated using the Scherrer equation with diffraction peak at $2\theta = 33.2°$.

H_2-TPR profiles of the prepared catalysts were carried out using a Micromeritics AutoChem 2910 equipped with a TCD detector. The catalyst sample (0.1 g) was loaded in a U-type quartz tube, purged with a flow of argon at 200 °C for 2 h to remove water or impurities, and then cooled to 60 °C. The TPR was conducted by heating the sample to 900 °C with a ramp of 10 °C/min in a gas mixture of 10 vol.% H_2/Ar (30 mL/min).

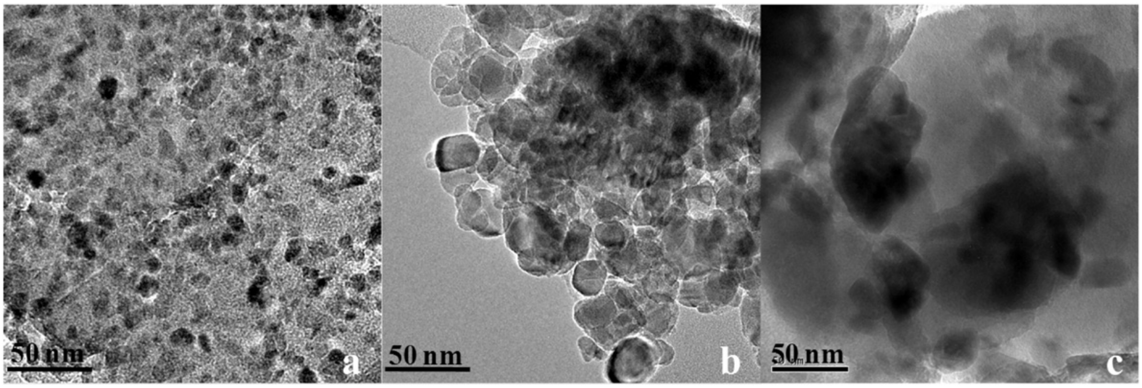

Fig. 1. TEM images of the as-prepared catalysts: (a) Fe/SiO_2; (b) Fe/TiO_2; (c) Fe/TS-1.

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