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Effect of iron loading on acidity and performance of Fe/HZSM-5 catalyst for direct synthesis of aromatics from syngas

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ABSTRACT

A bifunctional Fe/HZSM-5 catalyst was prepared for direct synthesis of aromatics from syngas. The influence of iron loading on acidity and syngas to aromatics (STA) performances over the Fe/HZSM-5 catalysts was studied. An increasing iron loading increased the amounts of active iron species, enhancing synergistic effect of active iron sites and HZSM-5 for the STA reaction. Higher iron loading in the Fe/HZSM-5 catalyst resulted in the decrease of Brönsted acid sites and increase of Lewis acid sites, promoting the formation of C_5^+ hydrocarbons and aromatics selectivity via weakening the cracking ability and enhancing the dehydrogenation property of HZSM-5. Excessive adding of iron loading induced the formation of graphitic carbon deposition, leading to a decrease of catalytic activity and stability.

1. Introduction

Syngas (CO/H_2) derived from biomass, coal, or natural gas can be converted to fuels [1,2] and chemicals [3,4] through Fischer-Tropsch synthesis (FTS) technology, which receives an increasing interest for both academic and industrial applications due to the environmental pollution and shortage of transportation fuels. However, hydrocarbon products are following the Anderson-Schulz-Flory (ASF) distribution, which restricts the efficient obtaining of specified products such as gasoline, diesel, jet fuels and so on. Numerous researchers make an effort to design suitable catalysts for breaking the ASF distribution via the adjusting of metal-support electronic and structure properties [5–7].

As an important basic material, aromatics produced mainly from petroleum cracking is utilized widely for synthesizing fibers, resins, rubbers and fine chemicals in the polymer industry [8–10]. With the rapid economy development and shortage of petroleum resource, new methods for aromatics synthesis from alternative carbon sources such as biomass and coal are demanded. Recently, syngas to aromatics (STA), methanol to aromatics (MTA) and methane

dehydroaromatization (MDA) processes are developed for the synthesis of aromatics. The direct conversion of methane to aromatics is thermodynamically limited. Even at high reaction temperature (about 700 °C), methane conversion is very low [11–13]. Methanol used for the MTA reaction must be synthesized separately from syngas through a methanol synthesis reaction [14]. Thus, direct conversion of syngas to aromatics is more favorable in view of thermodynamics and economics, which has attracted more and more attention [15,16]. A two-step process is firstly developed, in which syngas is converted into methanol, dimethyl ether, or olefins, and then further converted towards aromatics [17–19]. Recently, direct conversion of syngas into aromatics has been received a lot of attention, due to high energy and cost consumptions of the two-step process [20,21].

Syngas converting to aromatics via two intermediates (methanol or light olefins) is rapidly developed [22,23]. The Cu-Zn based catalyst is used to convert syngas into intermediate methanol (lower than 300 °C), and HZSM-5 is used as the catalyst for converting methanol to aromatics (higher than 400 °C). Due to the mismatch of operating temperature for both the catalysts, STA performances are suppressed obviously. In order to couple the operating conditions during the

processes of syngas to intermediate methanol or FTS light olefins and intermediate products to aromatics, many efforts have been devoted to optimize the catalysts. Combination of FTS catalysts with zeolite draws attention because of the matching of operating temperature for both the reactions. Compared to other FTS catalysts (including Co, Ru and Ni), the Fe-based catalyst is well suited for the conversion of lower H_2/CO ratio syngas derived from biomass or coal.

Chang et al. [24] reported firstly that the coupling of Fe based catalyst with zeolite promoted the formation of aromatic hydrocarbons. Recently, Ma et al. [25] designed a Na-Zn-Fe_5C_2 catalyst, which displayed high CO conversion and high alkenes selectivity. They combined the Na-Zn-Fe_5C_2 catalyst with hierarchical HZSM-5, which presented 51% aromatics selectivity under the stable state with over 85% CO conversion [23]. The influences of the composition and crystal size of ZSM-5 zeolite on direct conversion of syngas to gasoline-range iso-paraffins and aromatics have been studied [26]. Besides, the effect of metal active sites on the product distribution in the STA reaction has also been studied [21]. Yan et al. [27] prepared the Fe-Pd/HZSM-5 catalyst, and found that incorporation of Pd promoter improved the catalytic STA performances. The aromatics selectivity in C_5^+ hydrocarbons reached 45% under the optimizing reaction conditions. Guan et al. [15] adopted Ga promoter to modify the Fe-MnO/HZSM-5 catalyst, and found that the adding of Ga promoter promoted the dehydrogenation property, improving the formation of aromatics products. However, the Fe-MnO/GaZSM-5 catalyst deactivated rapidly with time on stream. The results of Plana-Pallejà et al. [28] indicated that the acidity and mesoporous properties of zeolite for the Fe/ZSM-5 catalyst had obvious influence on the selectivity of aromatics. Although a large number of studies are carried out on the influences of promoters, reaction conditions or zeolite properties for the composite Fe/ZSM-5 catalysts, the synergistic effect of Fe-HZSM-5 on the STA performances is still not understood.

Here, the effect of iron loading on acidity and STA performances of Fe/HZSM-5 catalysts were investigated in details. Because of the complexity of the Fe-HZSM-5 structures, several techniques, including inductively coupled plasma (ICP), N_2 isothermal adsorption-desorption (BET), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), NH_3 temperature-programmed desorption (NH_3-TPD), Raman spectra (LRS), Fourier transform infrared (FTIR) spectra and pyridine adsorption infrared spectroscopy (Py-IR) were used together to characterize the catalyst samples.

2. Experimental section

2.1. Materials and catalyst preparation

All the chemicals were used without further purification. Commercial HZSM-5 (HZ27) zeolite (SiO_2/Al_2O_3 ratio = 27) was purchased from Nankai University catalyst company. Before used, the zeolite was calcined in static air at 540 °C for 6 h.

Fe/HZSM-5 was prepared by incipient impregnation of HZSM-5 in $Fe(NO_3)_3$ solution, followed by evaporating the water at 80 °C. The powder was dried at 100 °C, and then calcined at 550 °C for 5 h. The resultant catalysts were named as x% Fe/HZ27 (Iron loading is x wt%).

2.2. Catalyst characterization

Textural properties of the catalyst samples were measured by N_2 physisorption at −196 °C using a Micromeritics ASAP 240 instrument. The specific surface area of the catalysts was calculated by Brunauer-Emmett-Teller (BET) method and the pore size distribution was analyzed by Barrett-Joyner-Halenda (BJH) method. The actual contents of Fe species were determined by inductively coupled plasma (ICP) on a Varian 720-OES.

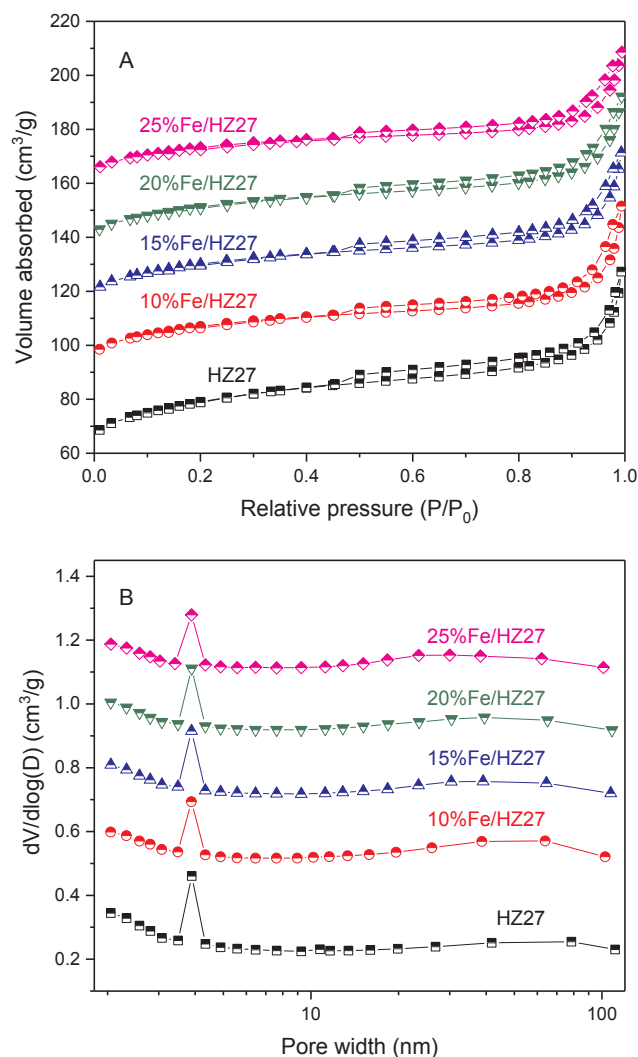Powder X-ray diffraction (XRD) patterns were recorded on a

Fig. 1. N_2 adsorption/desorption isotherms (A) pore size distribution (B) of the catalysts.

PANalytical X'Pert Pro diffractometer over the 2θ range of 5°–80°. XPS spectra of the catalysts were recorded on a Thermal XPS ESCALAB 250Xi Spectrometer with Al Kα X-ray source (1486.6 eV). The C 1s as a reference signal was adjusted to 284.6 eV.

Scanning electron microscopy (SEM) images were obtained on a QUANTA 400F scanning electron microscope to characterize the surface morphology of the catalysts. Transmission electron microscopy (TEM) experiments were performed in a TECNAI G2 F30 transmission electronic microscopy with 200 kV accelerating voltage.

The acid sites on the catalyst were determined by pyridine adsorption infrared spectroscopy (Py-IR). The measurements were performed on a Bruker VERTEX spectrometer. The FTIR analysis was performed on NICOLET 5700 FTIR Spectrometer. The acid amount and strength of the catalysts were measured by NH_3 temperature-programmed desorption (NH_3-TPD). The sample (100 mg) was pretreated with high purity N_2 at 500 °C for 1 h, and then cooled to 100 °C. Saturated adsorption of NH_3 on the sample was achieved by introducing 5% NH_3/N_2 into the system for 1.5 h. The sample tube was then purged with high purity N_2 to remove the physically adsorbed NH_3 until the baseline was stable, and then NH_3-TPD was performed in high purity N_2 by raising the temperature to 800 °C with a ramp of 10 °C/min. The desorbed NH_3 during the heating process was detected by a TCD.

Raman spectra (LRS) of the samples were measured using a RM-1000 Confocal Raman Microspectroscopy.