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Conversion of syngas toward aromatics over hybrid Fe-based Fischer-Tropsch catalysts and HZSM-5 zeolites

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ABSTRACT

Direct conversion of syngas (CO + H_2) toward aromatics has been demonstrated over a hybrid catalyst system composed of Fe-based FTS catalyst and HZSM-5 zeolite. Over the catalyst system, the aromatics were highly selective in the liquid hydrocarbon products with a content greater than 95%, and 70–90% of the aromatics were concentered on the toluene, xylene and 3C-branched alkylbenzenes. In this study, we systematically investigated the effects of reaction conditions (temperature, pressure, space velocity and H_2/CO ratio) and catalyst combination (Si/Al ratio of zeolite, weight ratio of HZSM-5 to Fe-based catalyst, metal modification of HZSM-5, and kind of Fe-based catalyst) on the CO conversion, selectivity to aromatics, aromatic distribution, and catalyst deactivation, combining with some characterization technologies (XRD, BET, NH_3-TPD, H_2-TPR, TG and ^{27}Al NMR). The obtained results show that HZSM-5 zeolite was the crucial component for aromatic formation. Excessive loading of the zeolite in bed would greatly suppress the carburization of reduced Fe into Fe carbides as well as CO dissociation on the Fe carbides because of the increasingly unfavorable direct contact between the acidic HZSM-5 and Fe-based catalyst, resulting in a remarkably lower CO conversion. HZSM-5 zeolite having high Brønsted acidity favored the formation of aromatics with a high content in liquid phase. However, as HZSM-5 had originally lower Brønsted acidity or the Brønsted acidity decreased during the aromatic synthesis due to more coke deposition, the selectivity to hydrocarbons in liquid phase gradually shifted to *iso*-paraffins rather than aromatics. Reactions operated over FeMn-HZSM-5 catalyst system at lower temperature or higher pressure led to an easier deactivation of HZSM-5 mainly from coke deposition. Compared with the FeMn-HZSM-5, FeK-HZSM-5 deactivated seriously at same conditions probably due to heavier and olefinic primary hydrocarbons over the FeK catalyst. In addition, ^{27}Al NMR showed that extraction of framework Al by *in situ* formed H_2O and CO_2 could be ignorable for the HZSM-5 deactivation. More detailed results and discussion from abundant experimental work on clarifying their effects on the aromatic synthesis can be found in the article.

1. Introduction

After light olefins (C_2–C_4) only, aromatics including benzene, toluene and xylene (BTX) are important and fundamental feedstocks for producing in bulk of plastic, pesticide, dye, solvent and *etc.*, and their market demand is growing steadily. More than 90% of aromatics, however, are produced from petroleum oil in the technologies of joint productions of light olefins and fuel, for example, catalytic reforming of naphtha and hydrocarbon pyrolysis [1,2]. Recently, the market share for producing of light olefins has been gradually occupied by non-petroleum resources, like coal-based methanol [3] and light alkanes separated from abundant shale gas [4], which certainly shocks the traditional oil-based olefin and aromatic markets. On the other hand, the concerns on the depletion of oil reserves have stimulated and driven more investigation of alternative and sustainable processes for production of aromatics, especially the BTX. CH_4 dehydroaromatization over Mo/HZSM-5 catalyst is a promising route for benzene formation due to extremely high selectivity to aromatics which can be greater than 80% [5]. Although the process has been verified by circulating fluidized bed reactor in laboratory [6], there are still big challenges in industry in solving of the rapid catalyst deactivation, raising one-pass CH_4 conversion and choosing of suitable reactor materials for high operation temperature (larger than 1073 K). Aromatization of light olefins and alkanes (C_2–C_8) over zeolites or metal-modified zeolites [7] is an optional industrialized process for replenishment of aromatics, but this process sacrifices the precious olefins products and its scale greatly depends on the supplying of alkanes resources from refinery plant. Coal, natural gas and biomass-based methanol-to-aromatic (MTA) process [8] has been widely focused on in recent years, and a 10,000 t/a pilot scale test was said to be run successfully in China. However, the

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profit of MTA process might be much sensitive to the relative price among coal, oil, methanol and aromatics in world market [9]. Paralleled to MTA process, dimethyl ether-to-aromatic (DMTA) [10] and other alcohols-to-aromatic, such as ethanol [11], sorbitol [12] and isobutyl alcohol [13], are also paid close attention to in recent years.

Instead of the process of syngas-methanol-aromatic, direct synthesis of aromatics from syngas (CO/H_2) would certainly be a more competitive route because of its short process flow in which one-pass CO conversion can reach 100% thermodynamically and the required H_2/CO ratio can be low (< 2) and the investment and cost in formation and separation of CH_3OH could be greatly cut down. Different from the Kölbel-Engelhardt (KE) process in which aromatic could be directly synthesized from CO/H_2O over Ni-based catalysts [14], for the traditional Fischer-Tropsch synthesis (FTS) from CO/H_2 over Fe-based and Co-based catalysts, however, rather than aromatics but olefin/paraffins and alcohols are the common formations [15–18], according to the FTS mechanism. Coupling of zeolite catalysts for further aromatization of the FTS products, therefore, seems to be necessary. Recently, several papers have dealt with the process using a dual-bed reactor system in which two catalysts of different functions placed in series [19–21]. For example, the syngas can be converted into aromatic-containing hydrocarbons in two separated reactors where one charged with Cu/Zn/Al_2O_3 catalysts and the other one with Mn-modified HZSM-5 zeolite *via* syngas-DME-aromatic at different conditions [19]. Also, combination of two different catalysts into a single reactor can lead the transformation of syngas into aromatics [22–25]. Early work by Guan et al. [22] reported a hybrid catalyst system of MnO supported Fe-based FTS catalyst and Ga/HZSM-5 catalyst for the reaction at mild conditions. Specially, the HZSM-5-supported Mo/HZSM-5 [26] and Pd-promoted Fe/HZSM-5 [27] catalysts can directly provide activity for synthesis of aromatics from syngas while the required operation pressures were relatively high (3.5–9 MPa) for obtaining of high CO conversion.

In fact, it is a basic idea of combination of FTS catalysts with HZSM-5 zeolite used for conversion of syngas into gasoline-ranged hydrocarbons, a mixture of *iso*-paraffins and aromatic [28,29]. However, it is much difficult to obtain high selectivity to aromatic as the main target, especially the BTX formations, over a hybrid catalysts system or a single catalyst, because the optimal conditions (temperature and pressure) for FTS and aromatization or isomerization reactions might not be matched well. For example, the working temperatures for FTS and aromatization over zeolite are suggested to be among 473–623 K and around 773 K, respectively. In this regard, the Co-based FTS catalysts could not be considered as the candidate for combination with zeolite in a single-bed reactor, because the optimal operating temperature for the catalyst in the FTS is lower than 523 K [30], and if the temperature is larger than 573 K the products are mainly C_1–C_4 alkanes, especially the CH_4. Therefore, Fe-based FTS catalyst seems to be the best choice in a single-bed reactor, and the high-temperature Fe-based FTS benefits its matching with the process of aromatic formation and a better recovery of the FT reaction heat for steam generation. Besides the basic reaction conditions including temperature, pressure, space velocity and the ratio of H_2/CO, the selectivity to aromatics and the aromatic distribution may essentially depend on the factors in catalyst combination, such as the Si/Al ratio of zeolite, weight of zeolite, and the kind of Fe-based catalyst. For Fe-based FTS catalysts, light olefins or/and paraffins are considered to be crucial to aromatic formation. In most cases, while alkali like K is an optional promoter for increasing the selectivity to olefins over Fe-based FTS catalysts, however, migration of the alkali to acid sites of zeolite due to alkali redistribution in the high-temperature FTS [31] could lower the activity of zeolite for aromatic formation [32]. Therefore, the kind of Fe catalyst with proper additives would be an important variable for obtaining of different olefin/paraffin ratios at different carbon number [33], and the formed hydrocarbons could show different activity toward aromatic over zeolites. Ideally, over a model catalyst or a hybrid catalyst system for achieving of a high selectivity to aromatic from syngas, it is expected that transition state species of hydrocarbons (C_2–C_5) formed at Fe active sites can move to Brønsted acid sites in the zeolite channels for completing of the aromatization rapidly, leaving little possibility for CH_4 formation and their excessive chain propagation.

Although a few of publications have shown the possibility of conversion of syngas into aromatic over a hybrid catalyst system [24,34,35] or in a dual-bed reactor system [19], design of an excellent catalyst still lacks of detailed information for demonstrating the effects of several factors on the aromatic formation and distribution. For example, the various Fe-based catalysts can provide variable selectivity to olefins and paraffins and on the other hand, may have negative interaction with zeolite as they combine. Therefore, in this study, we systematically investigated the effects of reaction conditions and catalyst combination on the aromatic synthesis over hybrid catalyst first. The aim of the study is to clarify their effects on the aromatic hydrocarbons synthesis for further flexible controlling of the aromatic formation and distribution and also for future catalyst design.

2. Experimental

2.1. Catalyst preparation

FeMn catalyst with a Fe/Mn wdieight ratio of 96:4 was prepared by co-precipitation of a solution of $Fe(NO_3)_3$ and $Mn(NO_3)_2$ using a precipitator of aqueous ammonia (1 mol/L) at a condition of pH = 8, T = 333 K and a continuous stirring. The resulting solution was allowed to stand at room temperature for 1 h, followed by filtering and washing with deionized water for 3 times, and then drying at 393 K for 12 h and calcination at 773 K for 5 h. The obtained powder was pressed, crushed and sieved into the particles with a size range of 250–425 μm for use. In addition, precipitated Fe was prepared using the same procedure above. Further, K was introduced to the Fe catalyst to prepare a 99.2Fe0.8K catalyst using incipient wetness impregnation (IWI) method [33,36]. Besides, a supported 10wt%Fe/TiO_2 also prepared using IWI method.

HZSM-5 zeolites with a Si/Al ratio range of 12.5–150 were supplied by Nankai University Catalyst Co., Ltd., China. 2 wt% Zn, Ga, Cu and Zr modified HZSM-5 (Si/Al = 12.5) catalysts were prepared by incipient wetness impregnation (IWI) method. The zeolites and modified zeolites were all calcinated at 773 K for 5 h before use.

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) patterns of samples were recorded on a Bruker AXS D8 Advance diffractometer using Cu Kα radiation (λ = 1.5406 Å) over a 2θ range of 5–90° at a scanning rate of 0.05°/s. BET surface areas of catalyst samples as well as their pore volumes were measured by BET method from N_2 adsorption at 87 K in a Micromeritics ASAP 2020 system. Prior to the adsorption measurements, all samples were vacuum-degassed at 673 K for 5 h to remove adsorbed moisture from their surfaces. Thermogravimetric (TG) analysis of spent HZSM-5 samples were carried out on a Mettler-Toledo TGA-1100SF Thermogravimetric analyzer for estimating coke amount in zeolite. ^{27}Al NMR spectrum of HZSM-5 and spent HZSM-5 samples were obtained on a Bruker AVANCE III 400 WB spectrometer at $B_0 = 9.4$ T. The corresponding resonance frequency of ^{27}Al was 104.3 MHz. Samples were packed in a 4 mm ZrO_2 rotor and spun at the magic angle (54.7°), and the spin rate was 12 kHz. Single pulse magic angle spinning spectra were acquired using a high power 0.4 μs pulse, corresponding to a tip angle of 15° and a recycle delay of 1 s. The ^{27}Al chemical shift was externally referenced to a 1.0 mol/L aqueous solution of $Al(NO_3)_3$.

NH_3 temperature programmed desorption (NH_3-TPD) profiles of catalyst samples were performed on a Chemstar automated chemisorption analyzer. A 100 mg sample of a catalyst was used for each test. The sample was first treated in a N_2 stream of 50 mL/min at 573 K for 3 h, cooled down to 323 K and subjected to a 2000 ppm NH_3/Ar stream