Low acidity ZSM-5 supported iron catalysts for Fischer–Tropsch synthesis

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ABSTRACT

Low acidity ZSM-5-supported iron catalysts were synthesized for use in Fischer–Tropsch conversion. Low acidity ZSM-5 was particularly chosen for its lower activity in respect to zeolite-acid catalyzed reactions (i.e. hydrocracking) which might lead to the lower selectivity for the light hydrocarbon and high selectivity for gasoline range components and for its high stability. Selective surface dealumination was also applied to zeolite and the resulting zeolite was used as a support for the catalyst in order to enhance its selectivity for gasoline.

Zeolite-supported catalysts were synthesized by using incipient wetness impregnation method and hybrid catalyst was prepared by physical admixing of ZSM-5 and base iron. The performances of catalysts prepared by two different methods were compared with respect to activity, selectivity and hydrocarbon yields. The catalytic activities of the catalysts were found to be considerably affected by the catalyst preparation method, percentage of iron in the catalyst and the reaction temperature. All catalysts displayed a CO conversion higher than 40% at 553 K. The selectivity toward C5–C11 hydrocarbons of catalyst prepared by impregnation method was determined to be 50–74%. The selectivity of the hybrid catalyst toward the same fraction was about 45%. No wax was detected in the products during the FT process using zeolite-supported iron catalysts. About 2 wt.% wax was measured in the FT products obtained by hybrid catalyst under similar conditions. Catalyst prepared with dealuminated zeolite displayed higher gasoline range hydrocarbon selectivity in comparison with catalysts having same iron content. Results of a 260 h time-on-stream test, carried out for one of the supported iron catalysts with 8 wt.% Fe, indicated that the catalyst was stable without any activity loss.

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1. Introduction

A major limitation of the Fischer–Tropsch (FT) technology is the low selectivity of the conventional catalysts toward targeted compounds. The well-known Anderson–Schulz–Flory (ASF) kinetics of the FT reaction imposes a limit to the maximum selectivity of 48% attainable for gasoline-range products [1,2]. The primary FT products can be upgraded by using down-stream conversion units enhancing the yield of the desired products. FT waxes can be evaluated as feedstock for catalytic cracking units (FCC) to produce high-octane gasoline with high content of isoparaffins and almost no aromatics [3]. Alternatively, waxes can be selectively hydrocracked to produce diesel fuel with high cetane number and improved cold flow properties [4].

The direct production of high octane gasoline through FT reactions is a great challenge related to catalyst development. This may be overcome by the use of metal/zeolite bifunctional catalysts, which can enhance the selectivity of the synthesis toward the desired products, i.e. gasoline range hydrocarbons [5–7]. In the FT process by these catalysts, the active metal (i.e. iron) phase catalyzes FT products consisted of wide range of hydrocarbons with considerable amount of heavy hydrocarbons. These first products are then converted into gasoline-range products through various mechanisms such as hydrocracking, olefin oligomerization, and branching that are induced by the zeolite component of the catalyst. On the other hand, the formation of heavy hydrocarbons is considerably hindered by zeolite due to its shape selectivity properties. Namely, the co-catalysts have higher selectivity toward gasoline-range products, indicating that they have double catalytic functions or bifunctionality.

The methods which have been used in synthesis of bifunctional FT catalysts based on zeolite and metals are the physical admixing [8,9], the conventional impregnation [10,11], ion-exchange [12] and adsorption of carbonyl complexes [13,14]. Direct synthesis of an aluminoferrisilicate zeolite [15] and preparation of encapsulated zeolite-FT catalysts [16,17] are the other alternative methods. The most commonly used methods are physical admixing and conventional impregnation. In most of the recent studies physical admixing was used for catalyst preparation [8,9,18]. However, the conventional impregnation could be a superior catalyst

preparation route over physical admixing, since it can result in a better dispersion of active component, a greater zeolite–metal interaction and a better utilization of shape selectivity of the zeolite structure.

The acidity, surface area, pore structure and cation exchange capability of the zeolite support are crucial factors affecting the catalytic performance of zeolite–metal FT catalysts with respect to aromatization, oligomerization, isomerization as well as alkylation reactions. By virtue of shape selectivity of zeolite, the chain-growth process is restricted to give low molecular weight products. Acidic nature of zeolite influences secondary hydrocracking and isomerization reactions, thereby producing more light, aromatic and branched hydrocarbons in the whole product portfolio. The efficiency and selectivity of a supported zeolite catalyst are closely related to the dispersion and particle size of the active metal component and to the nature of the interaction between the metal and the support. Supports with high surface area, like zeolites, generally yield well dispersed catalysts. A variety of zeolites such as ZSM-5 [6,8,9], zeolite Y [18,19], zeolite L [11], and beta [20] have been used in the synthesis of metal–zeolite FT catalysts. ZSM-5 seems superior with its acidic nature and shape selective properties. However, highly acidic catalysts suffer from high selectivities for undesired low molecular weight hydrocarbons due to their strong hydrocracking activities [21,22]. In addition, high acidity increases deactivation rates [23]. Zeolites with high alumina contents, as an indication of acidity, have difficulties in reducing metal oxides at cation exchange sites.

The acidity of zeolites can be reduced by dealumination process, thereby influencing the catalytic performance of the bifunctional FT catalysts. Preferential dealumination of acid sites on the external surface of the zeolite also can affect the stability of the catalysts against coking [24].

Iron, cobalt and ruthenium are well-known metals to be active for FT synthesis. Cobalt has been used in many zeolite-FT catalyst studies due to its low water gas shift activity and its convenience for production of heavier hydrocarbons mainly in the diesel range [25]. In order to obtain the desired reactions using zeolite catalysts, process temperatures need to be slightly higher than 573 K. However, at these temperatures, cobalt based bifunctional catalysts have very high methane selectivity [26]. The methane selectivity of iron catalysts at the same temperature level is lower. Furthermore, iron catalysts favor the production of primary olefins, which can be converted into the gasoline range hydrocarbons via zeolite in the bifunctional catalyst.

In this study, FT synthesis has been studied using bifunctional iron–low acidity ZSM-5 catalysts. A zeolite with very high silica to alumina ratio (SAR) of 280 due to its low acidity and cation exchange sites was used in the study. The purpose for choosing this zeolite was to take advantage of its shape selectivity while suppressing acid-catalyzed reactions like hydrocracking originating from its acidic nature. We aimed to reduce the light hydrocarbon selectivity and enhance the stability of the catalysts. In order to decrease role of the external surface which might favor hydrocracking reaction and to improve the internal surface utilization, zeolite was selectively dealuminated. In addition, dealumination reduces the aluminum content further and so the number of active sites for hydrocracking. Thereby, it was expected to have higher gasoline range hydrocarbon selectivity.

Iron was used in order to take the advantage of low methane and high olefin selectivity. The aim of the study was to maximize the gasoline yield with a stable catalyst. This paper presents the comparison of the two catalyst preparation routes with respect to activity, selectivity and hydrocarbon yields. The results of the catalytic activity of ZSM-5 supported iron catalysts with various iron percentages are given. Time on stream tests have been carried out for one of the catalysts. Finally, the effects of operation conditions on the FT reactions are given for temperature and the feed hydrogen to CO ratio.

2. Experimental

2.1. Catalyst preparation

The zeolite supported catalysts were prepared by the incipient wetness impregnation method. Ammonium form of ZSM-5 powder was provided by Zeolyst International Inc. It is a low acidity zeolite having a silica to alumina molar ratio of 280. ZSM-5 was used both as support and component of hybrid type catalysts. Iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) solution was used as the iron source. In the synthesis of the catalysts, ZSM-5 was impregnated with iron nitrate solution under continuous stirring. The impregnated catalysts were dried in the ambient air of 383 K overnight and then calcined at 723 K for 8 h. A ZSM-5 supported catalyst with a 4 wt.% iron was first synthesized and then it was used to prepare catalysts with 9 wt.% Fe and 18 wt.% iron by repeating the procedure mentioned above.

Base iron was prepared by precipitation method. Pure base iron was used as a catalyst in the FT activity tests and also used as a hybrid catalyst constituent. A promoted iron based catalyst was also prepared from the base iron catalyst via sequential impregnation of aqueous solutions of $Cu(NO_3)_2$ and K_2CO_3. The resulting composition of this catalyst is 100Fe7Cu3K. The details of synthesis procedure of the base iron and promoted iron catalysts were given elsewhere [27].

A hybrid catalyst was prepared by physical admixing of the base iron and ZSM-5. Both components were grinded, sieved to 250–350 mesh and then mixed completely.

The ZSM-5 zeolite was dealuminated by the following procedure. The zeolite was treated with 0.5 M oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) solution at 353 K under continuous stirring for 1 h. The resulting material separated from liquid phase via centrifuging was washed several times with distilled water, dried and calcined at 723 K for 8 h.

The ZSM-5 supported catalysts and hybrid catalyst were designated as SFeZ*X* and HFeZ*X*, respectively, where *X* is for the iron wt.% in the catalyst. Base iron catalyst and promoted iron based catalyst (conventional catalyst) were denoted as BFe and CFe, respectively, in the text.

2.2. Catalyst characterization

The synthesized catalysts were characterized by using X-ray diffraction (XRD), N_2 physisorption and inductively coupled plasma (ICP) techniques. X-ray diffraction (XRD) analyses were performed by using a XRD 6000 Shimadzu X-ray diffraction equipment with monochromatized Cu(Kα) radiation. The relative crystallinities of the ZSM-5 in the final catalysts were calculated from the XRD patterns, using the ASTM D5758 Standard. Hematite phase crystallite sizes were calculated by Scherrer's equation. BET surface area, the total pore volume and the pore size distribution of the catalysts were measured by N_2 physisorption at 77 K using a Quantachrome Autosorb Automated Gas Sorption System. The samples were degassed under vacuum at 393 K for 6 h prior to measurement. ICP analyses were carried out by Thermo Jorrel Ash Atom Scan 25 instrument in order to determine the wt.% of iron in the synthesized catalyst. The acidity of the zeolites was measured by using n-butyl amine adsorption and subsequent TGA measurements. TGA measurements were done on Mettler Toledo TGA/STDA851.