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Direct synthesis of isoparaffin by modified Fischer–Tropsch synthesis using hybrid catalyst of iron catalyst and zeolite

Yoshiharu Yoneyama, Jingjiang He, Yasuyuki Morii,
Shigeaki Azuma, Noritatsu Tsubaki *

Department of Applied Chemistry, School of Engineering, Toyama University, Gofuku 3190, Toyama 930-8555, Japan

Abstract

New hybrid catalysts for Fischer–Tropsch synthesis (FTS) to selectively produce isoparaffins at one step were developed by using Fe FTS catalysts mixed with H-ZSM-5 zeolite. The FTS catalysts produced normal paraffins, and then the normal paraffins isomerized and hydrocracked to produce isoparaffins on the zeolite in situ. For preparing highly active hybrid catalysts to lower methane formation, FTS catalysts based on Fe were developed. Carbon monoxide was the most effective reducing gas for the Fe FTS catalysts and the hybrid catalysts. Before adding the zeolite, the FTS products contained normal paraffins from C1–C16. After adding the zeolite, heavy hydrocarbons disappeared, and light hydrocarbons contained isoparaffins from C1 to C10 were produced alternatively. These results indicated that the hybrid catalyst composed of the mixture of Fe FTS catalysts and ZSM-5 zeolite had high performance for producing isoparaffins via one-step reaction.

Keywords: Fischer–Tropsch synthesis; Isoparaffin; Alkylate; Iron; Zeolite

1. Introduction

Fischer–Tropsch synthesis (FTS) is known as a method for producing clean liquid fuel from syngas. Because syngas is easily produced by organic resources such as natural gas, coal, and biomass, FTS is expected as a production method of liquid fuels instead of petroleum fuels. The FTS fuel contains large amounts of normal paraffins, which has high cetane number but with octane number near to 0. Thus the FTS fuel is suitable for diesel fuel, but not for gasoline. To obtain gasoline directly from syngas, zeolite can be employed to hydrocrack the FTS hydrocarbons to isoparaffins. As a commercial plant, only shell plant used a two-step process to produce branched hydrocarbons from syngas, where the 1st step is a conventional gas-phase FTS reaction, and the 2nd step is hydrocracking of the obtained waxy hydrocarbons after the removal of by-product, water, in a separate reactor. But this process is complicated, and its first step has a problem of catalyst deactivation due to the wax deposition onto the catalyst surface [1]. Though liquid-phase [2] and supercritical-phase [3] FTS can overcome catalyst deactivation problem derived from wax deposition, zeolite would decompose the hydrocarbon medium in the liquid-phase or supercritical-phase FTS reaction.

In the present study, hybrid catalysts composed of FTS catalyst based on iron and zeolite were developed to produce branched hydrocarbons from syngas at one step. FTS reactions were carried out under gas phase. In the FTS reaction, normal paraffins were produced on the FTS catalyst, and then the normal paraffins will be isomerized and hydrocracked on the neighboring zeolite in situ to produce isoparaffins. Furthermore, the heavy hydrocarbons such as wax can be decomposed easily on the zeolite surface [4], and the lifetime of hybrid catalyst is significantly extended. The hybrid catalysts as a mixture of cobalt FTS catalyst and ZSM-5 zeolite were developed [5–7], and the products contained much amounts of isoparaffins. It is known that the optimum temperature of Co FTS catalysts is around 513 K, and on the other hand that of zeolite is near 553 K [1]. Increasing reaction temperature of Co FTS catalyst tremendously enhances the selectivities of methane

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* Corresponding author. Tel.: +81 76 445 6846; fax: +81 76 445 6846.
E-mail address: tsubaki@eng.toyama-u.ac.jp (N. Tsubaki).

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and CO_2, which are not desired products. On the other hand, very low temperature will lower the activity of zeolites. The wide gap between the optimum temperatures of Co FTS catalyst and zeolite should be overcome. Considering the fact that the optimum reaction temperature of Fe FTS catalyst is about 553 K with high CO conversion as well as low CH_4 selectivity [1], it is expected that the hybrid FTS catalysts composed of Fe FTS catalyst and ZSM-5 zeolite have high activity for production of isoparaffin at one step by reducing methane formation. The present study evaluates the hydrocarbon products using hybrid catalyst for use of gasoline.

2. Experimental

2.1. Preparation of Fe FTS catalyst

$Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, KNO_3, and Na_2CO_3 were commercially available (Kanto Chemical) and used without further purification. In the precipitation reaction, 500 ml mixed aqueous solution of the metal nitrates, and 500 ml 4% sodium carbonate aqueous solution were added drop wise simultaneously to stirred hot water of 500 ml at 333 K and pH 8.0, and then the mixture was stirred for further 1 h. The precipitate was collected by filtration, and washed with distilled water (4× 300 ml) to remove sodium ion. The catalyst was dried at 298 K overnight, and calcined at 573 K for 4 h. The catalyst was ground to 20–40 mesh size particles. The composition of catalysts prepared in this study is summarized in Table 1.

2.2. Preparation of hybrid FTS catalyst

FTS catalysts prepared above were mixed with commercially available H-ZSM-5 zeolite ($SiO_2/Al_2O_3 = 83.7$, Sud Chemie, Japan) and then pressed at 60 MPa for 20 min. The generated hybrid catalysts were ground, and 20–40 mesh size particles were collected for FTS reaction.

2.3. FTS reaction

FTS reaction was carried out using a flow-type pressurized reactor. The catalysts of 0.5 g (Fe FTS catalyst base even for hybrid catalyst) were mixed with quartz sand of 0.5 g and put into the reactor. The catalysts were reduced with hydrogen, CO or syngas at 560 K under 1.0 MPa for 10 h in situ, and then FTS reactions were carried out using syngas ($H_2/CO = 1$) at 553 K with contact time (W_{Fe}/F) of 10 g h/mol. The gaseous products and the liquid hydrocarbon products from Fe FTS catalyst were analyzed online by gas chromatographs (GL-Science GC320, TCD and GL-Science GC390B, FID) with an active carbon column and a capillary column (Neutrabond-1), respectively. On the other hand, the gaseous and liquid hydrocarbon products using the hybrid FTS catalyst were analyzed online by the same gas chromatographs with an active carbon column and with a different capillary column (J&W Scientific, Alumina), respectively. The heavy hydrocarbons of Fe FTS catalyst were analyzed by gas chromatograph (Shimadzu GC-14B) with an SE-30 column. Argon was used as inner standard with 3% in the feed gas. In the case of hybrid catalysts, Fe FTS catalyst weight was the same to those reactions without zeolite, keeping W_{Fe}/F and Fe FTS catalyst weight the same in all reactions.

Table 1
Composition of FTS catalyst

Catalyst	Atomic ratio				
	Fe	Cu	Mg	Ca	K
Fe 1	100	1	300	30	10
Fe 2	200	2	300	30	10
Fe 3	200	6	300	30	10
Fe 4	200	10	300	30	10

3. Results and discussion

3.1. FTS catalysts activated at different reduction gas

CO conversion and products selectivity of FTS using Fe FTS catalysts are summarized in Table 2. For all catalysts prepared in this study, CO and syngas were found to be effective for reduction of FTS catalyst. CO conversions using CO or syngas as the reduction gas were larger than those using hydrogen. It is well known that iron carbide is one of the active species of the catalyst, and CO and syngas produce iron carbide to activate FTS catalyst [1,8]. Because syngas reduction was effective for the Fe FTS catalyst, syngas was selected as the reducing gas in this study.

In the Fe FTS catalysts, copper was added as a promoter for reduction of iron during reduction and reaction.

Table 2
Effect of reduction gas on catalytic activity and product selectivity

Catalyst	Reduction gas	CO conversion (%)	Selectivity (%)	
			CH_4	CO_2
Fe 1	H_2	27.0	9.0	25.5
	CO	58.2	8.9	30.7
	Syngas	79.6	9.8	35.1
Fe 2	H_2	28.1	9.5	26.6
	CO	80.8	11.4	32.7
	Syngas	73.3	10.1	33.1
Fe 3	H_2	38.6	10.1	29.0
	CO	69.6	9.6	32.4
	Syngas	68.9	8.4	29.3
Fe 4	H_2	33.7	9.8	26.4
	CO	96.4	13.8	57.3
	Syngas	96.4	13.1	42.6

Reduction: 573 K, 10 h; FTS conditions: $W/F = 10$ g h/mol; 553 K; 1.0 MPa; syngas: $H_2/CO = 1$.

Increasing copper content of the catalyst was expected to increase catalytic activity, however, the CO conversions of Fe 2 and Fe 3 catalysts decreased. The conversion of Fe 4 catalyst increased significantly. Because Fe 2 and Fe 3 catalysts contained less amount of copper than Fe 4 catalyst, reduction of iron in the catalysts might be not enough [9]. Since CO conversion of Fe 4 catalyst was the highest in the catalysts used, Fe 4 catalyst was used as the standard FTS catalyst for preparation of hybrid FTS catalysts.

3.2. Influence of reaction temperature on FTS reaction with Fe-based catalyst

As described above, the optimum reaction temperature of FTS catalyst based on Fe is about 553 K, and temperature higher than 553 K is desired for enhancing catalytic activity of ZSM-5 [1,7]. For preparing more light isoparaffins using hybrid FTS catalyst at one step, higher temperature than 553 K is desired. Influence of the temperature on FTS reaction using Fe 4 catalyst was investigated. The results of FTS reaction at 543, 553, 563 and 573 K were summarized in Table 3. Although CO conversion at 543 K was only 66.2%, CO conversions increased at higher temperature. Methane selectivity hardly changed and olefin/paraffin ratio of C6 hydrocarbon increased with the reaction temperature rising. At higher temperature, significant amount of olefin was formed. The yields of CO_2 decreased with increasing reaction temperature. These results indicated that water gas shift reaction was suppressed at higher temperature, obeying the thermodynamic rule of this reaction. Another possibility of CO_2 decreasing at higher temperatures might be the direct conversion of CO_2 to hydrocarbons via FTS-like reaction route. As expected, methane selectivity was low enough on Fe FTS catalyst even at 553–573 K, considering methane selectivity higher than 30% on some Co FTS catalyst at the same conditions.

3.3. Effect of zeolite addition on FTS selectivity

Hybrid FTS catalysts were prepared by mixing varied amounts of ZSM-5 zeolite and Fe FTS catalysts. The FTS results of hybrid catalyst are shown in Table 4. After the addition of ZSM-5 zeolite to Fe FTS catalysts, the CO conversions did not change so much, about 97%, due to the same Fe FTS catalyst weight even in hybrid system. For Fe 4-2 catalyst, the addition of twice amount of ZSM-5 slightly increased methane and CO_2 selectivity from 13.1 and 42.6 to 20.0 and 44.0%, respectively. Increased weight ratio of ZSM-5 to Fe FTS catalyst from 1 to 3 increased methane and CO_2 selectivity from 16.5 and 40.8% to 20.9 and 47.7%, respectively. FTS products on iron-based catalyst contain not only *n*-paraffin but also much α-olefins [1,10]. The α-olefins produced are re-absorbed not only on FTS catalyst itself but also on zeolite catalyst, decomposed to methane and *n*-paraffins [11]. Low diffusion rate inside channels of zeolite also enhances the decomposition possibility of α-olefins. Thus, the addition of ZSM-5 zeolite increased methane selectivity to some extent in the reactions using hybrid catalysts.

Table 3
Influence of reaction temperature on FTS reactivity using Fe 4 catalyst

Temperature (K)	CO conversion (%)	Selectivity (%)		Olefin/paraffin ratio (C6)
		CH_4	CO_2	
543	66.2	13.2	48.4	0.24
553	96.4	13.1	42.6	0.28
563	96.5	13.2	34.8	0.31
573	98.4	16.2	34.0	0.39

Reduction of catalyst: syngas ($H_2/CO = 1$); 573 K; 10 h; FTS reaction: catalyst, 0.5 g; $W/F = 10$ g h/mol; 553 K; 1.0 MPa.

Table 4
Effect of addition of ZSM-5 zeolite on FTS reactivity

Catalyst	Fe catalyst	ZSM-5 to Fe catalyst weight ratio	CO conversion (%)	Selectivity (%)	
				CH_4	CO_2
Fe 4	Fe 4	0	96.4	13.1	42.6
Fe 4-1	Fe 4	1	98.0	16.5	40.8
Fe 4-2	Fe 4	2	96.6	20.0	44.0
Fe 4-3	Fe 4	3	97.7	20.9	47.7

Reduction of catalyst: syngas ($H_2/CO = 1$); 573 K; 10 h; FTS reaction: Fe FTS catalyst, 0.5 g; $W/F(\mathrm{Fe}) = 10$ g h/mol; 553 K; 1.0 MPa.

Because hydrocarbons with longer chain are easily hydrocracked [4], wax produced on Fe FTS catalysts is quickly decomposed on zeolite to branched light hydrocarbons. The in situ decomposition of wax extended the lifetime of hybrid catalyst remarkably.

3.4. Hydrocarbon distributions on hybrid catalysts

Distributions of hydrocarbons from FTS reactions using zeolite hybrid catalysts, Fe 4-1, Fe 4-2, and Fe 4-3 catalysts, at 553 K are shown in Fig. 1. As a comparison, the results using Fe 4 catalyst only are also listed. For the Fe 4 catalyst, heavy normal paraffins up to C16 were produced. But after addition of H-ZSM-5, heavy normal paraffins disappeared, and much amounts of isoparaffins were formed on hybrid catalysts. Increased amount of ZSM-5 lightened the FTS products. For Fe 4-3 catalyst, C10 hydrocarbons disappeared and C4 yield increased significantly. In our previous papers, Co based zeolite hybrid FTS catalysts using ZSM-5 were already examined. In the FTS reactions using Co FTS hybrid catalyst, much amounts of isoparaffins were formed, however, the obtained hydrocarbons on Co hybrid catalyst were heavier than hydrocarbons using Fe hybrid catalysts here [5–7]. Although hydrocarbons on Co FTS hybrid catalyst were distributed up to C16, the hydrocarbons using Fe FTS hybrid catalyst here were limited to C10. In addition, the selectivity of C4–C6 branched hydrocarbons was very large on Fe FTS hybrid catalyst. On the other hand the selectivity of C4–C8 was large on Co FTS hybrid catalyst. The selectivities of C8 hydrocarbons were about 7.5% for the Co hybrid catalyst, but less than 1% for Fe hybrid

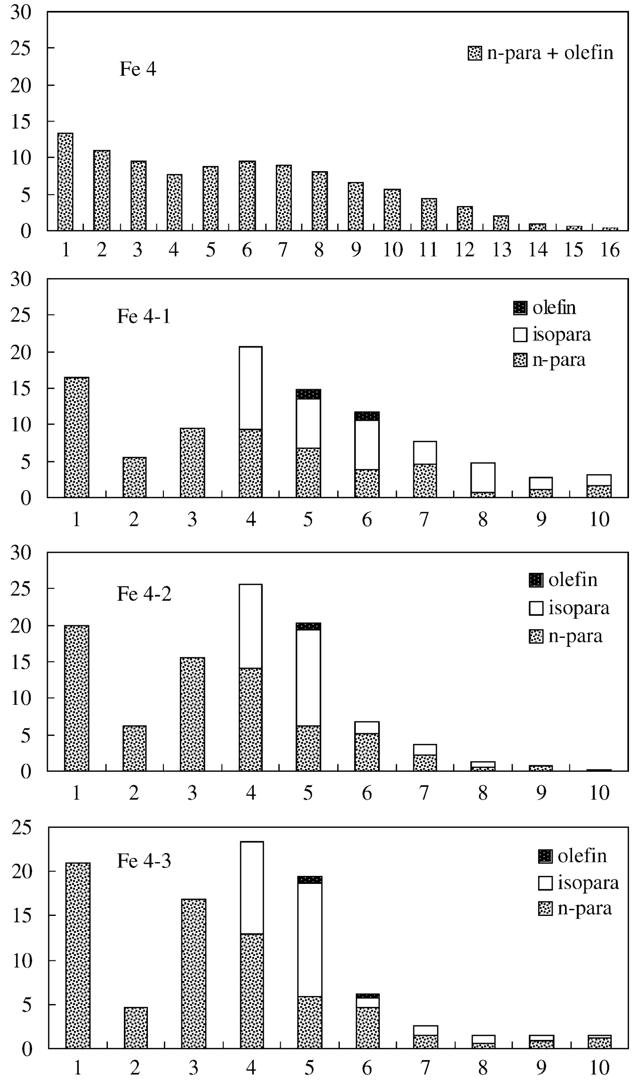

Fig. 1. Hydrocarbon selectivity of Fe 4/ZSM-5 zeolite hybrid catalyst. Catalyst composition (weight ratio), Fe 4-1: ZSM-5/Fe 4 = 1; Fe 4-2: ZSM-5/Fe 4 = 2; Fe 4-3: ZSM-5/Fe 4 = 3. FTS reaction: catalyst, 0.5 g (Fe catalyst base); *W*/*F*(Fe) = 10 g h/mol; 553 K; 1.0 MPa.

catalyst (Fe 4-2, Fe 4-3). As mentioned above, the optimum reaction temperature of Fe FTS catalysts was about 553 K, and at this temperature the hydrocracking and isomerization activity of *n*-paraffins on zeolite was high. Therefore, the hydrocarbons of FTS reaction using Fe hybrid catalysts became lighter and concentrated. Furthermore, Co FTS catalyst produced much amount of CH_4 when the temperature of its hybrid catalyst was higher than 513 K. But Fe FTS catalyst including hybrid catalyst showed low CH_4 selectivity intrinsically, increasing C4–C6 isoparaffin selectivity.

These findings indicated that the hybrid catalysts containing Fe FTS catalysts and H-ZSM-5 had high performance for production of isoparaffin from syngas at one-step reactions, by suppressing methane formation, compared with Co FTS hybrid catalyst, as Fe FTS catalyst exhibited low methane selectivity at high but optimum reaction temperature of the coexisting zeolite.

4. Conclusions

In order to selectively produce isoparaffins from syngas at one-step FTS reaction, new hybrid catalysts containing Fe FTS catalyst and ZSM-5 zeolite were developed. Syngas was the most effective reducing gas for the Fe FTS catalysts and used for reduction of the hybrid FTS catalysts. Before adding zeolite, FTS products mainly contained normal paraffins with long chain from C1 to C16. After adding the zeolite, heavy hydrocarbons disappeared, and light hydrocarbons from C1 to C10 rich in isoparaffins were produced. Methane selectivity of Fe hybrid catalyst was very low, compared with Co hybrid catalyst at the same conditions, as Fe FTS catalyst had low CH_4 selectivity at higher temperature such as zeolite's best reaction temperature. These results indicated that the hybrid catalysts containing Fe FTS catalysts and H-ZSM-5 for producing isoparaffins at one-step reaction were very effective.

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