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Semi-indirect synthesis of LPG from syngas: Conversion of DME into LPG

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Abstract

Efficient conversion of dimethyl ether (DME) into liquefied petroleum gas (LPG) with a hybrid catalyst is a novel method for semi-indirect synthesis of LPG fuel from syngas. The hybrid catalysts consisting of zeolite and hydrogenation catalyst were investigated in a fixed bed reactor. Experimental results demonstrated that the hybrid catalyst consisting of (Pd/SiO_2) and USY efficiently converted DME into LPG and restrained decomposition of DME into CO and H_2. With that catalyst, the one through conversion of DME reached about 100%, almost no CO and CO_2 were produced and selectivity for LPG was more than 65%.

Keywords: LPG; DME; Methanol; Syngas; Zeolite; Hybrid catalyst

1. Introduction

As the reserve of crude oil is shrinking and its price is steadily increasing recently, the efficient utilization of natural gas, especially remote natural gas reserves has been a highlight of research works. Compared with direct utilization through directly converting natural gas into chemical products, indirect conversion of natural gas via syngas (H_2/CO), ‘‘gas-to-liquids’’ (GTL), is much successful [1–5], and liquid products such as methanol, dimethyl ether (DME) and synoils have already been commercially produced, while the syngas has been produced commercially by steam reforming of natural gas or gasification of coal and biomass [6]. Production of liquefied petroleum gas (LPG), from syngas (synthesis gas, CO/H_2) is an important technology to convert nature gas into higher-value-added product. LPG, a general description of propane and butanes, either stored separately or together as a mixture, with the environmentally benign characteristics has been widely used as a clean fuel, chemical feed and a propellant for aerosols. Three methods for synthesis of LPG: direct synthesis of LPG from syngas; indirect synthesis of LPG from syngas, synthesis of methanol or DME from syngas, conversion of methanol or DME into hydrocarbon of LPG fraction (olefin and paraffin), and then olefin hydrogenation to LPG; semi-indirect synthesis of LPG from syngas, synthesis of DME from syngas or methanol and conversion of DME into LPG in presence of hydrogen. Differently from F-T synthesis technology [1,7,8], LPG can be synthesized directly from syngas over hybrid catalysts composed of methanol synthesis catalyst and zeolite [9,10]. The syngas can be converted into hydrocarbons through an intermediate of methanol or DME in the reaction.

DME is a new, non-toxic and clean fuel as a LPG alternative and could be synthesized from syngas or methanol [11]. Although DME’s physical properties are similar to LPG, instruments and specification for its application, transportation and storage should be modified and adjusted when it is used as LPG alternative for household cooking and heating. In other option, the efficient conversion of DME into LPG will promote DME commercial application.

We have reported that LPG could be synthesized from DME and hydrogen over the hybrid catalyst consisting of hydrogenation catalyst and zeolite [12]. In this work, we

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studied the catalytic synthesis of LPG from DME over a series of hybrid catalysts based on modified zeolite and hydrogenation catalyst in a fixed bed reactor and the efficient catalysts for LPG synthesis were presented.

2. Experimental

Three types of catalysts were used in this reaction: H-zeolite, hybrid catalyst and modified zeolite. The hybrid catalyst was prepared by mixing zeolite with methanol synthesis catalyst (Cu-Zn, commercial methanol catalyst, or Pd-Ca/SiO_2) and hydrogenation catalyst (Mo-Ni, Co-Mo and Co-Mo-Ni, commercial hydrotreating catalyst, or Pd-Ca/SiO_2). Pd-Ca/SiO_2 containing 4 wt% Pd and 0.75 wt% Ca was prepared by wetness incipient impregnation method. Zeolites ZSM-5, USY and β-zeolite were protoned-type zeolites. The ratios of silica to alumina in ZSM-5 and β-zeolite were 40 and 37, respectively. USY(10), USY(20) and USY(30) presented protoned ultra stable Y-type zeolite with silica/alumina ratio of 10, 20 and 30, respectively. Pd-ZSM-5 and Pt-ZSM-5, containing Pd and Pt (0.5 wt%), respectively, were prepared by method of ion exchange with the ammonia solution of palladium or platinum chloride. Pd/ZSM-5, containing the same weight of Pd, was prepared by method of incipient wetness impregnation method. The hydrogenation catalyst Pd/SiO_2 contained 0.5 wt% Pd. Pd/SiO_2 was prepared by incipient wetness impregnation method. SiO_2 used as a support for hydrogenation catalyst was commercially available one (Fuji Silysia Chemical Ltd.) with a specific surface area of 820 m^2/g.

The reaction feed is a mixture of DME and hydrogen. DME vapor was brought into the reactor through hydrogen. The ratio of hydrogen to DME in the feed was controlled by the temperature of the DME cylinder. A pressurized type of reaction apparatus with a fixed bed reactor was used for this study. The apparatus was equipped with an electronic temperature controller for a furnace, a tubular reactor with an inner diameter of 6 mm, thermal mass flow controllers for gas flows and a back-pressure regulator. The calcined catalyst power was shaped by suppressing to a disk, crushing and sieving to a size with 20/40 mesh. 1 g of catalyst was placed in the tubular reactor; inert glass sand was placed above and under the catalyst. The catalyst containing Cu-Zn was activated in a flow of 5% hydrogen in nitrogen at 300 °C for 4 h, the others was activated at 400 °C for 2 h in a pure hydrogen flow. All the products from the reactor were withdrawn at gaseous state and analyzed by gas chromatography (GC) on line. Details of the reaction procedures and the product analysis have been described elsewhere [7,12].

3. Results and discussion

Like methanol to hydrocarbon, DME can be converted into hydrocarbon over zeolite. The reaction is expressed as following:

$$CH_3OCH_3 \rightarrow \text{olefin} + \text{paraffin} + H_2O \qquad (1)$$

Also, differently from Fischer–Tropsch synthesis reaction mechanism that the product hydrocarbons followed Anderson–Schulz–Florry distribution, an LPG fraction was synthesized directly from DME over a hybrid catalyst composed of hydrogenation catalyst and zeolite.

The characteristics of zeolite played the main role for the conversion of DME and the distribution of hydrocarbon product. As Table 1 shows, when the zeolites (USY or ZSM-5)

Table 1
Results of synthesis LPG from DME over modified zeolite or hybrid catalyst consisting of methanol catalyst and zeolite

	Catalyst						
	USY (30)	ZSM-5	Cu-Zn USY (20)	Cu-Zn β-zeolite	Cu-Zn ZSM-5	Pd-Ca/SiO_2 β-zeolite	Pd-Ca/SiO_2 ZSM-5
Reaction temperature (°C)	340	350	340	350	350	350	350
Conversion of DME (%)	20.5	63.3	99.9	100.0	99.6	100.0	100.0
Product yield (*C*%)							
Hydrocarbons	20.5	63.2	68.9	67.5	57.3	64.3	63.3
CO_2	0.0	0.0	16.0	19.7	13.9	18.5	19.0
CO	0.0	0.1	15.0	12.8	28.3	17.1	17.6
Hydrocarbon distribution (*C*%)							
C_1	1.3	1.0	4.4	1.8	2.6	9.3	11.8
C_2^{2-}	8.2	13.0	0.0	0.0	0.0	0.0	0.0
C_2°	0.2	4.5	5.1	1.6	18.2	1.0	12.5
C_3^{2-}	13.0	15.9	0.0	0.0	0.0	0.0	0.0
C_3°	21.1	13.9	19.7	16.3	37.7	20.7	39.5
C_4^{2-}	12.3	7.4	0.0	0.0	0.0	0.0	0.0
C_4°	10.8	12.4	55.8	50.9	15.0	50.8	19.7
C_5	10.8	21.2	10.9	13.6	9.5	10.6	9.4
C_{6+}	22.3	10.8	4.1	15.8	17.1	7.5	7.1
LPG ($C_3 + C_4$)	57.2	49.6	75.5	67.2	52.7	71.5	59.1

Note: W/F = 9, 2.1 MPa, H_2/DME = 3.

Table 2
Results of synthesis LPG from DME over hybrid catalyst based on hydrotreating catalyst and USY

	Catalyst		
	Mo-Ni	Co-Mo	Co-Mo-Ni
		USY (20)	
Conversion of DME (%)	85.9	91.3	92.2
Product yield (*C*%)			
Hydrocarbons	82.6	90.4	87.9
CO_2	2.3	0.5	3.3
CO	1.0	0.4	1.0
Hydrocarbon distribution (*C*%)			
C_1	32.9	17.3	32.6
C_2	8.4	10.0	8.6
C_3	8.9	9.6	8.4
C_4	20.2	28.0	20.8
C_5	14.7	19.3	14.2
C_{6+}	15.0	15.8	15.5
LPG ($C_3 + C_4$)	29.1	37.6	29.1

Note: W/F = 9.0, 2.1 MPa, 350 °C, H_2/DME = 3.

were employed as the catalyst, a mixture of olefin and paraffin as the product was gotten and DME conversion were not high. As the content of heavy hydrocarbons (containing more than five carbon atoms) is high, the zeolite lost its activity quickly because of deposition of coke on the surface of catalyst. When the hybrid catalyst combined methanol synthesis catalyst with zeolite was employed, the DME conversion reached almost 100%, and the olefins in product were hydrogenated into paraffins. The hybrid catalyst (Cu-Zn/USY) had the highest selectivity for LPG (more than 75%).

USY and β-zeolite with large pore size (7.4; 7.6 × 6.4 Å) had higher selectivity for LPG than the ZSM-5 with small pore size (5.6 × 5.3 Å). The hybrid catalyst based on (Pd-Ca/SiO_2) produced higher selectivity for methane fraction than the catalysts based on Cu-Zn. This was attributed to high activity of hydrogenation over palladium.

Unfortunately, a considerable part of DME decomposed into CO over the hybrid catalyst, and some CO was converted into CO_2 by shift reaction. The reaction routs are following:

$$\text{Olefin} + H_2 \rightarrow \text{paraffin} \tag{2}$$

$$CH_3OCH_3 + H_2O \rightleftharpoons 2CO + 4H_2 \tag{3}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{4}$$

As Table 2 demonstrates, when the methanol synthesis catalyst in hybrid catalyst was replaced by the Mo-Ni, Co-Mo or Co-Mo-Ni catalyst, the decomposition of DME was restrained, but the DME conversion and selectivity for LPG was low. Also, the yield of heavy hydrocarbons was high, which would cause the catalyst deactivated quickly.

After ZSM-5 was modified by ion exchanging Pd or Pt into the zeolite, as Table 3 shows, its performance in the reaction of synthesis of hydrocarbons from DME showed remarkable change. There was no olefin found in the product, because the intermediate olefins produced from DME were hydrogenated in situ catalyzed by Pd or Pt metal. So the activity of the zeolite was promoted. The main hydrocarbons in the product were ethane, propane and butane. The yield of methane was very low, especially when using Pd-ZSM-5. With that catalyst, the DME conversion reached about 100%, and almost no CO and CO_2 were produced and selectivity for LPG was more than 50%. Although Pt-ZSM-5 had small higher selectivity than Pd-ZSM-5, it produced more unfavorable product CO, CO_2 and methane.

Pd-USY(20) and Pd-β-zeolite modified by addition of Pd into the zeolite through ion exchange, showed a high activity for deposition of DME to CO and hydrogenation of CO to methane. Thus, the selectivity for LPG was much low.

Table 4 demonstrates the effect of metal content in catalyst based on modified ZSM-5 by addition of the metal of VIIIB group. For both catalyst Pd-ZSM-5 and Pt-ZSM-5, the content of LPG fraction in hydrocarbon changed little

Table 3
Results of synthesis LPG from DME over modified zeolite

	Catalyst			
	Pd-ZSM-5	Pt-ZSM-5	Pd-USY(20)	Pd-β-zeolite
Conversion of DME (%)	100.0	100.0	89.5	94.1
Product yield (*C*%)				
Hydrocarbons	98.2	94.5	74.4	73.6
CO_2	0.4	2.4	0.2	0.1
CO	1.4	3.0	14.9	20.5
Hydrocarbon distribution (*C*%)				
C_1	1.8	2.7	94.9	96.4
C_2	29.2	29.9	0.8	1.0
C_3	33.4	40.2	2.0	1.8
C_4	17.3	14.3	0.6	0.3
C_5	11.3	7.7	0.3	0.1
C_{6+}	7.2	5.2	1.4	0.3
LPG ($C_3 + C_4$)	50.6	54.4	2.6	2.1

Note: W/F = 9.0, 2.1 MPa, 350 °C, H_2/DME = 3.

Table 4
Performance of modified ZSM-5 by VIIIB metal

	Catalyst							
	Pd-ZSM-5 0.1[a]	Pd-ZSM-5 0.2[a]	Pd-ZSM-5 0.5[a]	Pd/ZSM-5 0.2[a]	Pd/ZSM-5 0.5[a]	Pt-ZSM-5 0.1[a]	Pt-ZSM-5 0.2[a]	Pt-ZSM-5 0.5[a]
Conversion of DME (%)	99.6	100	100	100	100	100	100	100
Product yield (*C*%)								
Hydrocarbon	99.1	99.6	99.3	98.4	95.7	98.1	97.5	93.8
CO_2	0.1	0.2	0.2	0.1	0.3	0.2	0.3	3.8
CO	0.8	0.2	0.5	1.5	4.0	1.7	2.2	2.4
Hydrocarbon distribution (*C*%)								
C_1	1.8	2.2	2.1	1.3	5.3	1.6	1.6	2.8
C_2	23.7	25.8	27.6	27.6	26.6	28.3	26.2	32.0
C_3	29.3	28.0	29.7	31.2	35.6	32.7	31.2	38.9
C_4	22.1	20.3	21.2	21.0	17.8	19.2	17.9	14.6
C_5	11.5	14.2	12.6	12.5	10.3	9.8	10.4	7.5
C_{6+}	11.6	8.4	6.8	6.5	3.4	8.5	12.7	4.2
LPG ($C_3 + C_4$)	51.4	48.4	50.9	52.2	53.4	51.9	49.1	53.5

Note: W/F = 9.0, 2.1 Mpa, 375 °C, H_2/DME = 3.

[a] Pd content (wt%).

with different metal content in zeolite. But the ratio of propane to butanes increased with the increase in the metal content. The modified ZSM-5 with high metal content produced a low yield of heavy hydrocarbons. Thus, the modified ZSM-5 with high metal content would have high stability for the reaction. With the modified ZSM-5 (Pd-ZSM-5), the DME conversion reached almost 100%, almost no CO and CO_2 were produced and the selectivity for LPG was more than 50%.

Compared with Pt-ZSM-5, Pd-ZSM-5 had a better selectivity for hydrocarbons and LPG, because the yields of unfavorable product CO, CO_2 and methane are lower, although Pt-ZSM-5 had little higher LPG content in hydrocarbon product than Pd-ZSM-5.

Pd/ZSM-5, prepared by incipient wetness impregnation method, had a higher selectivity for CO and methane than Pd-ZSM-5 that was prepared by ion exchange method, which resulted in high yield of CO and methane.

The hybrid catalyst consisting of Pd/SiO_2 and USY had the highest selectivity to LPG and a very low selectivity for CO among the catalysts tested in this work. Table 5 demonstrates the effect of the ratio of silica to alumina in USY and weight ratio of hybrid catalyst. The USY(20) with silica/alumina ratio of 20 had the highest selectivity to LPG. Experimental results indicated that zeolite in hybrid catalyst played the main role for distribution of product hydrocarbons. The high activity of USY-zeolite was attributed to its suitable acidity essential for formation of hydrocarbons.

Table 5
Performance of hybrid catalyst (Pd/SiO_2)/USY in LPG synthesis reaction

	Catalyst				
	(Pd/SiO_2)/USY (10) 1:2[a]	(Pd/SiO_2)/USY (20) 1:2[a]	(Pd/SiO_2)/USY (20) 1:1[a]	(Pd/SiO_2)/USY (20) 2:1[a]	(Pd/SiO_2)/USY (30) 1:2[a]
Conversion of DME (%)	100.0	100.0	99.8	69.4	99.8
Product yield (*C*%)					
Hydrocarbons	95.6	97.3	96.9	63.4	97.1
CO_2	0.0	0.0	0.0	0.0	0.0
CO	4.3	2.7	3.0	5.9	2.7
Hydrocarbon distribution (*C*%)					
C_1	2.0	3.2	1.7	81.4	4.5
C_2	15.4	12.2	15.0	0.8	11.1
C_3	25.4	25.6	25.4	0.9	24.5
C_4	35.0	39.5	36.1	3.1	39.8
C_5	15.1	12.8	15.1	1.4	12.9
C_{6+}	7.2	6.6	6.7	12.3	7.0
LPG ($C_3 + C_4$)	60.4	65.2	61.5	4.1	64.3

Note: W/F = 9.0, 2.1 MPa, 375 °C, H_2/DME = 3.

[a] Weight ratio of (Pd/SiO_2)/USY.

The high selectivity for LPG was attributed to three dimensions structure and large pore size (7.4 Å). Olefins (propylene and butenes) in product hydrocarbons formed in the cage of zeolite would easily leave the active site and diffused to the surface of catalyst Pd/SiO_2 for hydrogenation reaction. Hydrogenation of olefins would stop the growth of carbon chain and decrease the yield of heavy hydrocarbons (containing more than five carbon atoms) and coke. The zeolite would lose its activity quickly because of deposition of coke on the surface of catalyst.

That high ratio of silica to alumina in resulted in a high selectivity to methane was attributed strong acidity of USY with high ratio of silica to alumina. High content of Pd/SiO_2 in hybrid catalyst resulted in high activity for decomposition of DME into CO and H_2. Also, the low content of USY would result in low DME conversion and high selectivity for heavy hydrocarbon, because of no enough active sites for DME conversion. Thus, the suitable hybrid catalyst for synthesis of LPG from DME was (Pd/SiO_2)/USY with the weight ratio of 2 and USY zeolite with the silica to alumina ratio of 20.

4. Conclusion

When the zeolite (USY or ZSM-5) were employed as the catalyst, a mixture of olefin and paraffin as the product was gotten and DME conversion were not high. If the hybrid catalyst that consisted of methanol synthesis catalyst and zeolite was employed, the DME conversion and LPG content in hydrocarbon products were satisfactory; while a considerable part of DME had decomposed into CO and CO_2. The replace of catalyst methanol synthesis catalyst with Mo-Ni, Co-Mo or Co-Mo-Ni in hybrid catalyst could restrain the decomposition of DME in to CO, but the DME conversion and selectivity for LPG were not high.

VIIIB metal (Pd or Pt) supported on ZSM-5 as catalyst restrained decomposition of DME and the DME conversion was also high. The catalyst made by method of ion exchanging was better than by method of wetness impregnation.

The highly efficient catalyst for synthesis of LPG from DME was (Pd/SiO_2)/USY. (Pd/SiO_2)/USY as catalyst restrained decomposition of DME into CO, and the DME conversion was also high. With that catalyst, the DME conversion reached almost 100%, almost no CO and CO_2 were produced, and selectivity for LPG was more than 65%.

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