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Direct synthesis of LPG fuel from syngas with the hybrid catalyst based on modified Pd/SiO_2 and zeolite

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Abstract

A novel method to synthesize LPG fuel directly from syngas with a hybrid catalyst is presented. The new hybrid catalyst, consisting of ($Pd–Ca/SiO_2$) and β-zeolite, showed a high activity and selectivity for LPG fraction. It also showed a higher stability than Cu–Zn/USY at high reaction temperature. The sintering of palladium metal was main contribution to the deactivation of the hybrid catalyst ($Pd–Ca/SiO_2$)/β-zeolite.

Keywords: LPG; Palladium; Hybrid catalyst; Hydrocarbon; Methanol

1. Introduction

Since the first energy crisis, researchers and commercial corporations have put much attention on the efficient utilization of natural gas, especially on remote natural gas reserves. Liquefied natural gas (LNG) was proved feasible but suffered from the cost of production, storage and transformation. The way of directly converting natural gas into products is still far from the feasible. Indirect conversion of natural gas via syngas (H_2/CO), 'gas-to-liquids' (GTL) as Fig. 1 shows, is much successful [1–5], and liquid products such as methanol, DME (dimethyl ether) and synoils have been commercially produced. Liquefied petroleum gas (LPG), a mixture of propane and butanes, has environmentally benign characteristics and widely been used as a clean fuel. Production of LPG from natural gas is an important option for the efficient conversion of natural gas into higher value-added products. As we have reported [6,7], differently from Fischer–Tropsch synthesis reaction mechanism [8–11] that the hydrocarbons of products follow Anderson–Schulz–Flory distribution, an LPG fraction was synthesized directly from syngas over a hybrid catalyst composed of methanol synthesis catalyst and zeolite. The syngas, which is produced commercially by steam reforming of natural gas or gasification of coal and biomass [12], can be converted into hydrocarbons through methanol or DME as an intermediate in the reaction. The hybrid catalyst that composed of Cu–Zn methanol synthesis catalyst and Y-type zeolite showed a good initial activity and selectivity for the synthesis of LPG. However, as well known, the Cu–Zn catalyst deactivated under an atmosphere of CO_2 and water at high temperature [13,14], so the stability of the hybrid catalyst need to be improved. In recent years, supported palladium as catalysts for synthesis of methanol has been studied extensively. In particular, effect of supports, precursors of palladium, alkali, alkali-earth and rare earth elements as promoters have been investigated deeply [16–21].

In the present work, we investigated the performance of the hybrid catalyst based on supported Pd and zeolite for the selective synthesis of LPG from syngas, and a highly stable and active hybrid catalyst is presented.

2. Experimental

2.1. Catalyst preparation

The hybrid catalyst employed in this study consisted of a zeolite and a methanol synthesis catalyst based on Pd/SiO_2.

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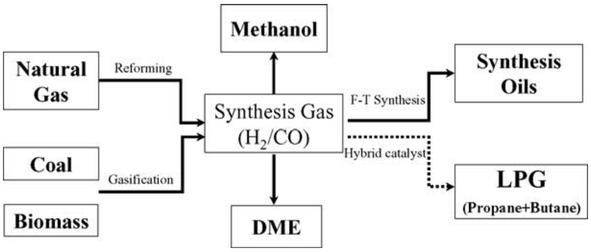

Fig. 1. GTL process scheme.

Two methods for preparing the hybrid catalysts were powder mixing and granule mixing. The powder mixing was that the required weight of Pd methanol catalyst and zeolite were ground together, mixed finely, pressed into a disk, crushed, and then sieved to particles with a size of 20–40 mesh. Granule mixing was that Pd methanol catalyst and zeolite were shaped into particles with the above size, respectively, and then mixed finely as the weight ratio required by experiments before loading into the reactor.

The zeolites, USY and β, were pretreated to became the proton-typed before using to prepared the hybrid catalysts. The ratios of silica to alumina in the two zeolites were 12.2 and 37.1, respectively.

The Pd/SiO_2, containing 4 wt.% of Pd, was prepared by incipient wetness impregnation method. The physical characteristics of silica supports are showed in Table 1, and the precursors and contents of Pd and Ca in methanol synthesis catalyst can be found in Table 2. A commercial silica (Fuji Silysia Chemical Ltd.) was impregnated with an aqueous solution of palladium salt, dried at 393 K, and then calcined at 723 K for 8 h in a sequence. Calcium-promoted Pd catalyst (Pd–Ca/SiO_2), containing 4 wt.% of Pd and 0.75 wt.% of Ca, respectively, was prepared by impregnating Pd/SiO_2 above mentioned with an aqueous solution of calcium salt, drying and calcining with the same procedure.

2.2. Apparatus

A pressurized flow type reaction apparatus with a fixed bed reactor was used for the experiment of LPG synthesis from syngas. 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. One gram of catalyst was loaded in the reactor and inert glass sand was placed above and below the catalyst. The catalyst was dried at 523 K in a flow of nitrogen for 2 h, and activated in a flow of hydrogen at 673 K for 3 h. All the products from the reactor were sampled at gaseous state and analyzed by gas chromatography (GC) on line. Details of the reaction procedures and product analysis have been described elsewhere [6,7].

Table 1
The specific surface area and pore volume of silica supports

Silica	Q15	Q6	Q3	G3
Specific area (m^2/g)	200	450	550	820
Pore volume (ml/g)	1.00	0.50	0.30	0.45
Average pore diameter (nm)	15.0	6.0	3.0	2.2

2.3. Measurement of palladium dispersion

Palladium dispersion in the catalysts was estimated by hydrogen chemisorption on the metal. The uptake of hydrogen chemisorption was measured by hydrogen chemisorption isotherm on an ASAP 2010 Adsorption Instrument (produced by Micromeritics Instrument Corporation). The procedure for the hydrogen chemisorption is as follows: (1) evacuation of the catalyst sample at 298 K for 30 min to remove air; (2) evacuation of the catalyst sample at 298 K for 30 min to remove water; (3) reduction in flowing hydrogen (30 cm^3 min^{-1}) while heating with temperature programming (10 K min^{-1}) to 673 K and holding at 673 K for 1 h; (4) evacuation for 1 h at 673 K to remove gas phase and adsorbed hydrogen followed by cooling in vacuo to 373 K; and (5) measurement of hydrogen uptake.

2.4. X-ray diffraction (XRD)

The samples of zeolite, silica and catalysts were ground into powder and pressed into a disk. The X-ray diffraction profiles were recorded with a RINT 2000 System (Rigaku) diffractometer with Cu Kα radiation. The energy was 40 kV × 20 mA.

3. Results and discussion

The mechanism of hydrocarbon synthesis from synthesis gas over the hybrid catalyst was different from F–T reaction mechanism. The hydrocarbon formation followed as the route below:

$$CO + H_2 \rightleftharpoons CH_3OH \xrightarrow{-H_2O} CH_3OCH_3 \xrightarrow{-H_2O} \text{hydrocarbons} \qquad (1)$$

The hybrid catalyst has two functions: methanol synthesis and conversion of methanol into hydrocarbons. In this

Table 2
The precursors and compositions of methanol synthesis catalysts

Methanol catalyst	Pd/Q3 (A)	Pd/Q3 (B)	Pd–Ca/Q3 (A)	Pd–Ca/Q3 (B)	Pd–Ca/Q3 (C)
Precursor of Pd	$PdCl_2$	$Pd(NO_3)_2$	$PdCl_2$	$Pd(NO_3)_2$	$Pd(NO_3)_2$
Content of Pd (wt.%)	4.0	4.0	4.0	4.0	4.0
Precursor of Ca			$CaCl_2$	$CaCl_2$	$Ca(NO_3)_2$
Content of Ca (wt.%)			0.75	0.75	0.75

hybrid catalyst system, methanol from synthesis gas over methanol synthesis catalyst was converted into DME and then hydrocarbons over zeolite. Production of a considerable amount of CO_2 accompanied with the formation of DME and hydrocarbon because of water–gas shift reaction. The hydrocarbons synthesis from synthesis gas involves following reactions (the reaction enthalpies are calculated at the standard condition, 298 K and 1 atm):

$$CO + 2H_2 \rightleftharpoons CH_3OH - 91.03\ \mathrm{kJ/mol} \qquad (2)$$

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O - 22.67\ \mathrm{kJ/mol} \qquad (3)$$

$$CH_3OCH_3 \rightarrow \text{hydrocarbons} + H_2O \qquad (4)$$

$$H_2O + CO \rightleftharpoons CO_2 + H_2 - 41.12\ \mathrm{kJ/mol} \qquad (5)$$

The total reaction is as follows:

$$2n\mathrm{CO} + (n+1)\mathrm{H}_2 \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{CO}_2 - \sim 210n\ \mathrm{kJ/mol}, \qquad (6)$$
$$(n = 1, 2, \ldots, 6)$$

Because of the synergetic effect of methanol synthesis catalyst and zeolite, hydrocarbon yield broke the limit of the equilibrium of methanol formation from syngas and could reach a high level at low reaction pressure. Usually, the reaction temperature of conversion of methanol or DME into hydrocarbons was higher than 573 K, but at that high temperature Cu–Zn methanol synthesis catalyst suffered from deactivation with time on stream in an environment where water and CO_2 co-existed. The supported palladium catalyst for methanol synthesis showed a more stable activity than Cu–Zn methanol catalyst [16,17], and addition of calcium into supported palladium promoted its activity [15]. The high activity of hybrid catalyst based on supported palladium is important for commercial application of direct synthesis of LPG from syngas.

3.1. *Effect of calcium promoter as well as the precursor of calcium and palladium*

A group of hybrid catalysts were prepared by powder mixing of Pd methanol catalyst and zeolite according to the weight ratio of 1/1. The precursors of palladium and calcium employed in the catalysts were chloride and nitrate. As Table 3 shows, hybrid catalysts based on Pd/SiO_2 had low activity for synthesis of LPG from syngas. Addition of calcium into Pd/SiO_2 increased the activity and selectivity for LPG of hybrid catalyst obviously. Precursors of palladium and calcium have an evident influence on the performance of catalyst. The hybrid catalysts prepared from palladium nitrate and calcium nitrate had a higher activity than those from their chlorides. The experimental results demonstrated that Cl^- anion deteriorated the activity of hybrid catalyst. Precursors of palladium and calcium did not have a significant influence on distribution of product hydrocarbons (C mol%, the mole percent of carbon atoms in hydrocarbons). This was because characteristics of the zeolite in hybrid catalyst played the main role for distribution of product hydrocarbons. The β-zeolite employed in hybrid catalyst has a higher activity and selectivity for LPG synthesis than USY zeolite.

3.2. *Influences of palladium dispersion*

A group of catalysts Pd–Ca/SiO_2 (C), modified Pd methanol synthesis catalysts, were prepared with silica supports with different specific surface area. Palladium dispersion in the catalysts was estimated by hydrogen chemisorption. Fig. 2 shows their performance combined with β-zeolite as hybrid catalysts. CO conversion and hydrocarbon yield increased with the value of palladium dispersion while the selectivity for LPG ((C3 + C4)% in hydrocarbons) keeping almost constant. This means that the high dispersion of Pd metal supported on silica benefited the activity of hybrid catalyst for synthesis of hydrocarbons.

Table 3
Results of LPG synthesis from syngas by using hybrid catalysts

Catalyst	Pd/Q3 (A) USY	Pd–Ca/Q3 (A) USY	Pd–Ca/Q3 (B) USY	Pd/Q3 (A) β-zeolite	Pd/Q3 (B) β-zeolite	Pd–Ca/Q3 (B) β-zeolite	Pd–Ca/Q3 (C) β-zeolite
Conversion of CO (%)	2.7	7.5	15.0	5.5	4.1	21.8	33.5
Product yield (C mol%)							
Hydrocarbons	2.1	4.6	9.9	6.0	3.6	12.1	19.2
DME	0.0	0.0	0.0	0.0	2.0	0.0	0.0
CO_2	0.6	2.9	5.1	0.4	0.0	9.7	14.3
Hydrocarbon distribution (C mol%)							
C1	19.4	8.5	5.7	55.1	23.5	2.0	3.4
C2	18.9	16.8	21.2	6.4	15.9	11.7	7.8
C3	36.3	41.3	35.2	22.2	32.8	39.1	40.3
C4	18.9	24.7	27.8	12.9	22.4	34.1	36.0
C5	6.5	7.4	8.5	2.4	5.2	11.4	9.8
C6+	0.0	1.3	1.7	0.0	0.0	1.8	2.7
C3 + C4	55.2	66.1	62.9	35.1	55.3	73.2	76.3

2.1 MPa, $H_2/CO = 2$, 623 K, W/F = 9.0 g h/mol (based on total weight of Pd catalyst and zeolite), (Pd catalyst)/zeolite = 1/1 (by weight, powder mixing).

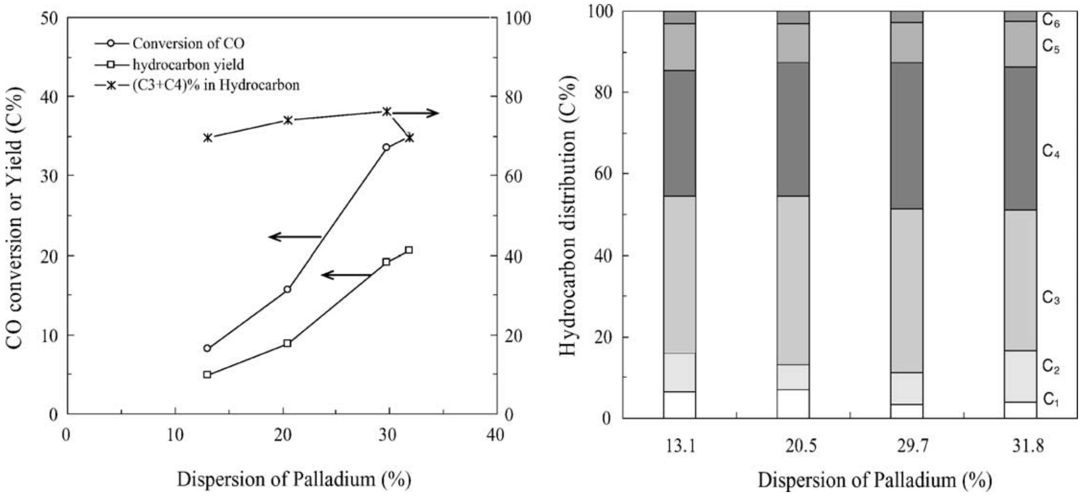

Fig. 2. The performance of (Pd–Ca/SiO$_2$)/β-zeolite as a function of specific surface area of silica 2.1 MPa, H$_2$/CO = 2, 623 K, W/F = 9.0 g h/mol (based on total weight of Pd catalyst and zeolite), (Pd–Ca/SiO$_2$)/β-zeolite = 1/1 (by weight, powder mixing).

Because high dispersion of Pd supported on silica would be more active for methanol formation [10], this enhanced the yield of hydrocarbons from syngas. The characteristics of zeolite employed have main role on distribution of hydrocarbon product.

3.3. Effect of weight ratio of hybrid catalyst (Pd–Ca/SiO$_2$)/β-zeolite

The composition of hybrid catalyst (Pd–Ca/SiO$_2$)/β-zeolite affected the conversion of synthesis gas and selectivity of products. As Table 4 shows, the selectivity for LPG hydrocarbons increased when the weight ratio of Pd–Ca/SiO$_2$ to β-zeolite increased. The high weight ratio also resulted in a higher CO conversion. That was attributed to the formation rate of methanol from synthesis gas was the rate-determining step in the total process of synthesis of hydrocarbons. Considering the composition of LPG product and stability of hybrid catalyst, the weight ratio of Pd–Ca/SiO$_2$ to β-zeolite = 2/1 was suitable for this reaction.

Table 4
Effect of zeolite amount on LPG synthesis of from syngas

(Pd–Ca/G3(C))/β-Zeolite	1:1	2:1	3:1
Conversion of CO (%)	35.0	43.5	43.5
Product yield (C mol%)			
Hydrocarbons	20.6	25.1	23.7
DME	0.0	0.0	0.0
CO$_2$	14.5	18.4	19.8
Hydrocarbon distribution (C mol%)			
C1	3.8	4.1	5.2
C2	12.7	9.1	6.5
C3	34.7	37.6	41.2
C4	34.9	36.1	35.8
C5	11.4	10.6	8.8
C6+	2.5	2.6	2.5
C3 + C4	69.6	73.7	77.1

2.1 MPa, H$_2$/CO = 2, 623 K, W/F = 9.0 g h/mol (based on total weight of Pd catalyst and zeolite).

3.4. Effect of reaction pressure

Compared with Cu–Zn/USY [6,7], (Pd–Ca/SiO$_2$)/β-zeolite had a lower activity for LPG synthesis from syngas. As Fig. 3 shows, the increase in reaction pressure promoted the CO conversion and yield of hydrocarbons with decreasing the selectivity for LPG a little. Also, the yield of methane decreased at high reaction pressure. This is favorable because methane is the most unfavorable product in this process. That the low CO conversion resulted in lighter hydrocarbons could be attributed to the cracking of long chain hydrocarbon on the surface of zeolite. So the medium reaction pressure (4.0–6.0 MPa) was suitable for the LPG synthesis from syngas using the hybrid catalyst of (Pd–Ca/SiO$_2$)/β-zeolite.

3.5. Effect of reaction temperature

Table 5 shows CO conversion, yield of products and hydrocarbon distribution at different reaction temperatures. When the reaction temperature was raised, C$_1$ and C$_3$ hydrocarbons increased and C$_2$, C$_4$, C$_5$ and C$_{6+}$ hydrocarbons decreased. Both CO conversion and selectivity for LPG reached the maximum at 648 K. Because the Pd methanol catalyst had a lower activity than Cu–Zn [20], a high reaction temperature was needed for the enough reaction rate of methanol formation for LPG synthesis over the hybrid catalyst. But the high reaction temperature was not favored by equilibrium yield of methanol from syngas, and the rate of methanol formation was the reaction control for hydrocarbon synthesis from synthesis gas over hybrid catalyst. Low concentration of methanol and DME, as intermediates from synthesis gas to hydrocarbons, would restrict the rate of hydrocarbon formation. Thus high

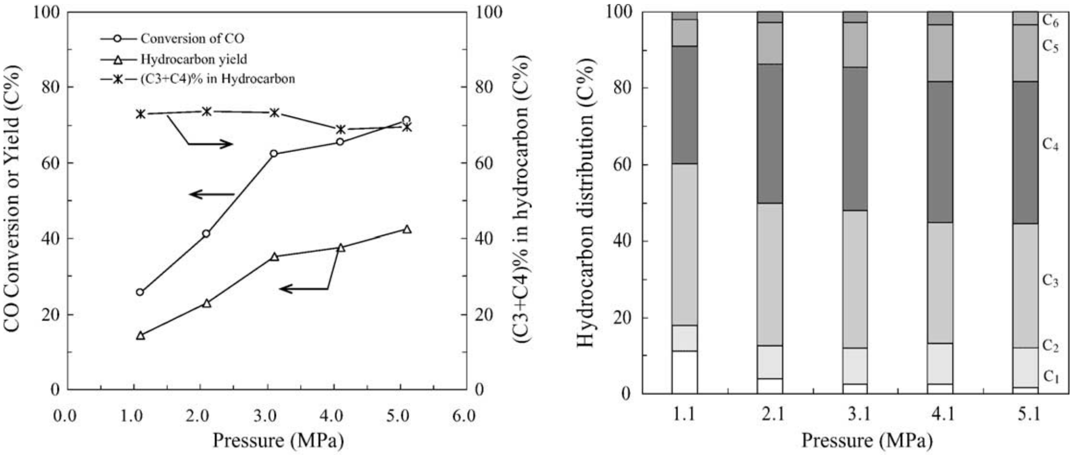

Fig. 3. The performance of (Pd–Ca/Q3(C))/β-zeolite as a function of reaction pressure $H_2/CO = 2$, 623 K, W/F = 9.0 g h/mol (based on total weight of Pd catalyst and zeolite), (Pd–Ca/SiO_2)/β-zeolite = 2/1 (by weight, powder mixing).

reaction temperature decreased the CO conversion and selectivity for LPG. Temperature also had a great effect on distribution of hydrocarbon products. Because supported Pd acted as a hydrogenation catalyst, there were no olefins found in the hydrocarbon products. At low temperature, the average molecular weight of the product hydrocarbons was larger than that at high temperature, where direct hydrogenation of CO into methane catalyzed by Pd resulted in the high yield of methane. Also, high temperature enhanced cracking rate of C_4–C_{6+} hydrocarbons, resulting in the decrease of content of heavy hydrocarbons in products. So the appropriate temperature of reaction was about 648 K.

3.6. Stability of hybrid catalysts

Fig. 4 compared the performances of three hybrid catalysts: Cu–Zn/USY (1/1 by weight, powder mixing), (Pd–Ca/G3)/β-zeolite (2/1 by weight, powder mixing) and (Pd–Ca/G3)/β-zeolite (2/1 by weight, granule mixing). The hybrid catalyst Cu–Zn/USY demonstrated high activity and more than 75% selectivity for LPG at the initial stage of reaction at 608 K and 2.1 MPa, but its CO conversion decreased about 40% after 52 h of time on stream. The two hybrid catalysts based on palladium, (Pd–Ca/G3)/β-zeolite, had higher one through conversion of CO than Cu–Zn/USY. Furthermore, the activity of hybrid catalyst (Pd–Ca/G3)/β-zeolite decreased with time on stream more slowly than that of Cu–Zn/USY. The hybrid catalyst (Pd–Ca/G3)/β-zeolite prepared by granule mixing had a slightly higher selectivity and much higher CO conversion than that prepared by powder mixing, and obviously its activity decreased more slowly than that of the other two catalysts. The supported palladium as methanol catalyst is more stable than that based on Cu and Zn oxides at high temperatures and high partial

Table 5
Influence of reaction temperature on LPG synthesis from syngas

(Pd–Ca/G3)/β-Zeolite			
Temperature (K)	623	648	673
Conversion of CO (%)	65.5	74.1	72.4
Product yield (C mol%)			
Hydrocarbons	37.7	40.7	41.1
DME	0.0	0.1	0.1
CO_2	27.8	33.3	31.2
Hydrocarbon distribution (C mol%)			
C1	2.5	7.2	15.4
C2	10.6	8.5	7.8
C3	31.6	42.6	48.2
C4	37.1	32.6	23.7
C5	14.8	7.1	3.8
C6+	3.5	2.0	1.1
C3 + C4	68.7	75.2	71.9

4.1 MPa, $H_2/CO = 2$, W/F = 9.0 g h/mol (based on total weight of Pd catalyst and zeolite), (Pd–Ca/G3(C))/β-zeolite = 2/1 (by weight, powder mixing).

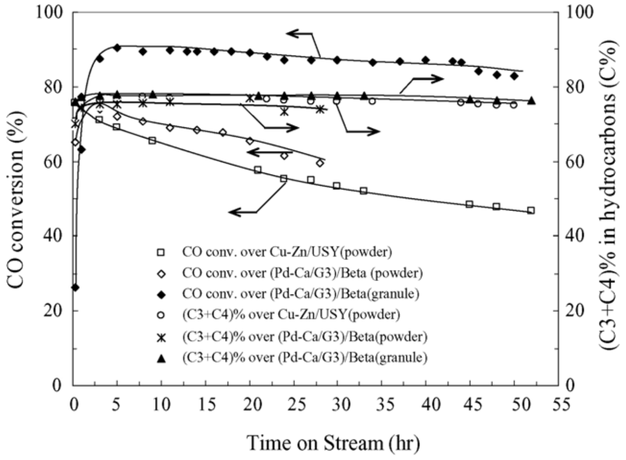

Fig. 4. The performance of hybrid catalyst as a function of time on stream (Pd–Ca/G3)/beta (granule mixing): 648 K, 5.1 MPa, W/F = 9.0 g h/mol, (Pd–Ca/G3)/beta (powder mixing): 648 K, 4.1 MPa, W/F = 9.0 g h/mol, Cu–Zn/USY(powder mixing): 608 K, 2.1 MPa, W/F = 4.5 g h/mol.

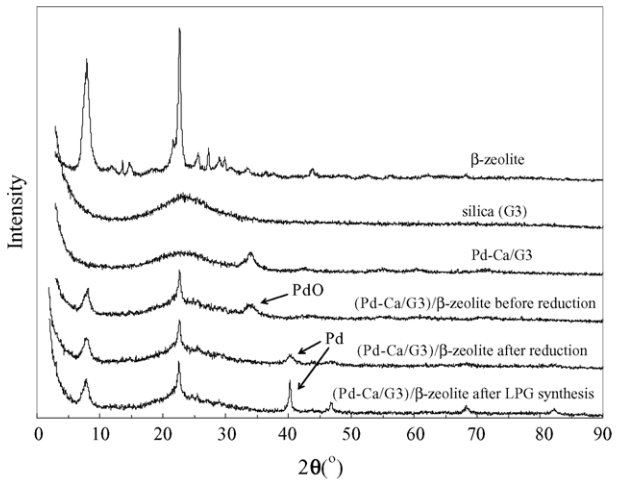

Fig. 5. XRD spectra of catalysts.

pressures of CO_2 and H_2O. The higher reaction temperature also decreased the yield of heavy hydrocarbons (containing more than five carbon atoms), which was deleterious for the activity of zeolite. On other hand, β-zeolite is more thermally stable than Y-type zeolite. Thus, the hybrid catalyst based on (Pd–Ca/G3) and β-zeolite has a higher stability than Cu–Zn/USY. For (Pd–Ca/G3)/β-zeolite, the catalyst prepared by granule mixing gave a higher selectivity and activity for LPG synthesis than the catalyst prepared by powder mixing. On the other hand, the catalyst prepared by granule mixing showed a much better stability than Cu–Zn/USY and (Pd–Ca/G3)/β-zeolite (powder mixing). Yoshie et al. also got a hybrid catalyst with a high selectivity and activity by granule mixing for hydrocarbon synthesis from CO_2 [22]. Granule mixing would decrease the sintering of palladium and formation of coke, resulting in high activity and stability of hybrid catalyst for LPG synthesis from syngas.

3.7. X-ray diffraction(XRD)

The samples of zeolite, silica (G3) and hybrid catalyst (Pd–Ca/G3)/β-zeolite were examined by X-ray diffraction to determine the chemical form and crystallite size. As Fig. 5 shows, the hybrid catalyst composed of supported Pd–Ca on silica (calcined) and β-zeolite showed a typical peak of PdO (1 0 1), and reduced hybrid catalyst showed a peak of metallic palladium (1 1 1) [23]. These findings demonstrated that palladium oxide was converted into palladium metal by hydrogen reduction. After reaction, the increased height of Pd metal peak proved the crystallite size of Pd metal increased. According to the Scherrer equation [$D = k\lambda/(\beta_d \cos\theta)$], the size of crystallites could be calculated. Slow scanning the peak of Pd(1 1 1) give the corresponding size of Pd metal, 10 and 22 nm, as shown in Table 6. On the other hand, the crystallite size of β-zeolite did not change during the reduction and reaction. Fig. 2 also indicated that high dispersion and small size of Pd resulted in high activity for LPG synthesis from syngas. Thus the increase of size of Pd metal crystallite was a major reason for the deactivation of hybrid catalyst (Pd–Ca/SiO_2)/β-zeolite.

Table 6
Data of XRD

Catalyst	(Pd–Ca/G3)/β-zeolite		
	Before reduction	After reduction	After LPG synthesis
Peak	PdO (1 0 1)	Pd (1 1 1)	Pd (1 1 1)
2θ(°)	33.836	40.118	40.118
Crystallite size (nm)	6.5	10	22

4. Conclusions

The high dispersion of Pd metal benefited the activity of hybrid catalyst. The medium reaction pressure was suitable for LPG synthesis from syngas using hybrid catalyst based on modified Pd/SiO_2 by calcium and β-zeolite. The hybrid catalyst consisted of (Pd–Ca/G3(C)/β-zeolite (granule mixing) showed higher stability and activity than Cu–Zn/USY and selectivity more than 75% for LPG fraction. This catalyst may enable the process of producing LPG from natural gas.

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