Catalysis Letters Vol. 102, Nos. 1–2, July 2005 (© 2005)
DOI: 10.1007/s10562-005-5202-x

A highly stable and efficient catalyst for direct synthesis of LPG from syngas

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Received 7 December 2004; accepted 18 February 2005

Liquefied petroleum gas (LPG) fuel was directly synthesized from syngas over a hybrid catalyst which contained a methanol synthesis catalyst and zeolite. The new hybrid catalyst composed of (Pd–Ca/SiO_2) and β-zeolite, showed a high activity and selectivity for LPG production. X-ray diffraction (XRD) characterization of the catalyst was used to analyze the deactivation of (Pd–Ca/SiO_2)/β-zeolite.

KEY WORDS: LPG; palladium; hybrid catalyst; methanol; hydrocarbon.

1. Introduction

As the reserve of crude oil is shrinking and its price is increasing, the efficient utilization of natural gas, especially the remote natural gas reserves, has been a highlight of research works. Production of liquefied petroleum gas (LPG), a mixture of propane and butanes, from the syngas is an important option to convert natural gas into a higher-value-added product, because LPG has environmentally benign characteristics and has widely been used as a clean fuel. Syngas conversion to methanol is limited by equilibrium. One way to increase conversion of syngas is to remove product methanol from the equilibrium as it formed. The production of hydrocarbons serves to relieve the thermodynamic constraints inherent to methanol synthesis by transforming methanol into hydrocarbons. Thus, synthesis of hydrocarbons from synthesis gas can be realized at low pressure and high temperature. As we have reported [1, 2], differently from F-T synthesis reaction mechanism [3–5], a mixture of low molecular weight hydrocarbons can be synthesized directly from syngas over hybrid catalysts composed of methanol synthesis catalyst and zeolite. The syngas, which is produced by reforming of natural gas or gasification of coal or biomass, can be converted into hydrocarbons through an intermediate of methanol or DME in the reaction. The hybrid catalyst composed of Cu–Zn methanol synthesis catalyst and Y-type zeolite showed a good initial activity and selectivity for synthesis of LPG. But, its stability needs to be improved because the Cu–Zn catalyst deactivates under an atmosphere of CO_2 and water at high temperatures [6, 7]. Supported palladium as catalysts for synthesis of methanol has been studied extensively. In order to get the catalyst with high activity, effect of supports, precursors of palladium, alkali, alkali-earth and rare earth elements as promoters have been investigated [8–14].

In the present paper, we report the performance of the hybrid catalyst, which is composed of a modified supported Pd catalyst and β-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 methanol synthesis catalyst based on Pd/SiO_2 and zeolite. The method of hybrid catalyst preparation is that Pd catalyst and zeolite were pelletized and crushed into particles with a size of 20/40 mesh, respectively, first, and then mixed finely as the weight ratio required by experiments before loading into the reactor. The zeolites, USY and β-type, were pretreated to became proton-type before used 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 atom, was prepared by incipient wetness impregnation method. A commercial silica (Fuji Silysia Chemical Ltd.) was impregnated with an aqueous solution of $Pd(NH_3)_2(NO_3)_2$, dried at 120 °C, and then calcined at 450 °C for 8 h in a sequence. The 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 $Ca(NO_3)_2$, drying and calcining with the same procedure [10].

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2.2. *Apparatus and procedures*

A pressurized flow 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 stainless tubular reactor with an inner diameter of 6 mm, thermal mass flow controllers for gas flows and a back-pressure regulator. One gram of hybrid catalyst was loaded in the reactor and inert glass sand was placed above and under the catalyst bed. The catalyst was dried at 250 °C in a flow of nitrogen for 2 h and activated in a flow of hydrogen at 400 °C for 3 h. All the products from the reactor were sampled in gaseous state and analyzed by gas chromatography (GC) on line. Details of the reaction procedures and product analysis have been described elsewhere [1].

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 25 °C for 30 min to remove air; (2) evacuation of the catalyst sample at 25 °C for 30 min to remove water; (3) reduction in flowing hydrogen (30 cm^3/min) while heating with temperature programming (10 °C/min) to 400 °C and holding at 400 °C for 1 h; (4) evacuation for 1 h at 400 °C to remove gas phase and adsorbed hydrogen followed by cooling in vacuo to 100 °C; and (5) measurement of hydrogen uptake.

2.4. *X-ray diffraction*

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

3. Results and discussion

The mechanism of hydrocarbon synthesis from synthesis gas over the hybrid catalyst is different from the F-T reaction mechanism. Hydrocarbons are formed by the following route:

$$\begin{aligned} &CO + 2H_2 \rightarrow CH_3OH \\ &\xrightarrow{-H_2O} CH_3OCH_3 \xrightarrow{-H_2O} \text{hydrocarbons} \qquad (1) \end{aligned}$$

The hybrid catalyst has two functions, that is, methanol synthesis and conversion of methanol into hydrocarbons. In this hybrid catalyst system, methanol formed 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 the formation of DME and hydrocarbon because of the water gas shift reaction. The overall reaction is expressed as following:

$$\begin{aligned} &2nCO + (n+1)H_2 \rightarrow C_nH_{2n+2} + nCO_2 \\ &\quad - \sim 210\,n\text{kJ/mol} \quad (n = 1, 2, \ldots, 6) \qquad (2) \end{aligned}$$

Although the equilibrium yield of methanol from syngas is very low at a temperature higher than 300 °C, because of the synergetic effect of methanol synthesis catalyst and zeolite, the yield of hydrocarbons breaks the limit of the equilibrium of methanol formation and can reach a high level at a high temperature and low reaction pressure.

3.1. *The performances of the hybrid catalysts Cu–Zn/USY and Pd–Ca/SiO$_2$*

Usually, the conversion of methanol or DME into hydrocarbon takes place at the temperature above 300 °C. However Cu–Zn methanol synthesis catalyst suffers from deactivation at this high temperature and its activity decreases with time on stream in environments where water and CO_2 co-existed. The supported palladium catalyst for methanol synthesis shows more stability but lower activity than Cu–Zn methanol catalysts [9,10], and addition of calcium into supported palladium promotes its activity [15].

As figure 1 shows, the hybrid catalyst Cu–Zn/USY (1/1 by weight) demonstrated a high activity and selectivity with more than 75% content of LPG fraction (C_3 and C_4 hydrocarbons) in total product hydrocarbons at the initial stage of reaction. But its activity decreased quickly with time on stream. The CO conversion decreased about one third after 30 h. The hybrid catalyst (Pd–Ca/SiO_2)/β-zeolite (2/1 by weight) showed a stable activity for LPG synthesis. Although its CO conversion was lower than Cu–Zn/USY, stability was much higher, and the LPG selectivities of the two catalysts were almost the same. Thus the hybrid catalyst Pd–Ca/SiO_2/β-zeolite is promising if its activity can be improved, because the high activity of hybrid catalyst is important for commercial application of the direct synthesis of LPG from syngas.

3.2. *Effect of specific surface area of silica support*

A group of Pd–Ca/SiO_2 catalysts were prepared by the impregnation method with different kinds of silica supports with different specific surface area of silica. Palladium dispersion in the catalysts was estimated by hydrogen chemisorption. Table 1 gives their characteristics, and figure 2 shows their performance combined with β-zeolite as hybrid catalysts. CO conversion and hydrocarbon yield increased with the value of specific surface area of the supports while the selectivity for

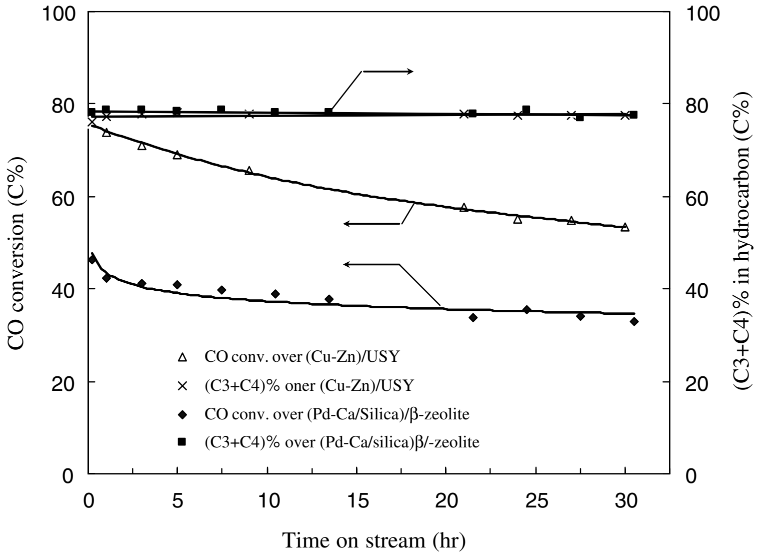

Figure 1. The performance of hybrid catalysts as a function of time on stream, Cu–Zn/USY: 330 °C, 2.1 MPa, W/F = 4.5 g h/mol, (Pd–Ca/G3)/β-zeolite: 350 °C, 2.1 MPa, W/F = 9.0 g h/mol.

LPG ((C_3 + C_4) % in hydrocarbons) was almost constant. This means that the high dispersion of Pd metal supported on silica benefited the activity of hybrid catalyst for synthesis of hydrocarbons. Because high dispersion of Pd on supported on silica would be more active for methanol formation, this enhanced the yield of hydrocarbons from syngas. The characteristics of zeolite employed play the main role on distribution of hydrocarbon product.

Table 1
The characteristics of methanol synthesis catalysts

Catalyst: silica	Pd–Ca/Silica			
	Q15	Q6	Q3	G3
Specific area (m^2/g)	200	450	550	820
Dispersion of palladium (%)	13.1	20.5	29.7	31.8
Pore volume (ml/g)	1.00	0.50	0.30	0.45
Average pore diameter (nm)	15.0	6.0	3.0	2.2

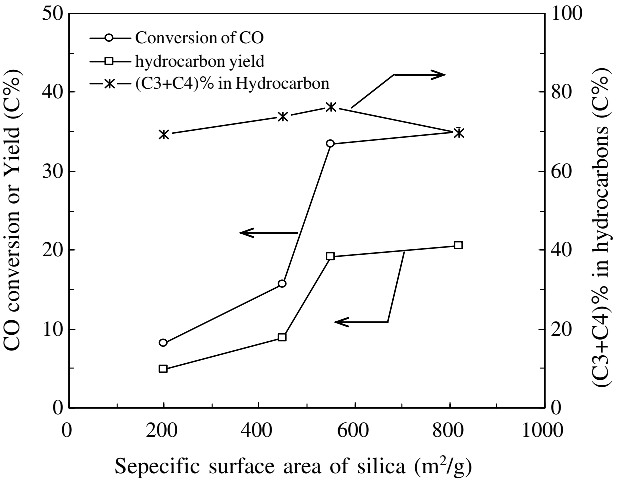

Figure 2. The performance of (Pd–Ca/SiO_2)/β-zeolite as a function of specific surface area of silica, 2.1 Mpa, H_2/CO = 2, 350 °C, W/F = 9.0 g h/mol, (Pd–Ca/SiO_2)/β-zeolite = 1/1 (by weight).

3.3. Effect of reaction pressure

Compared with Cu–Zn/USY, (Pd–Ca/SiO_2)/β-zeolite had a lower activity for LPG synthesis from syngas. As table 2 shows, a higher total reaction pressure promoted the CO conversion and yield of hydrocarbons, with only a slight decrease in the selectivity for LPG. Also, the yield of methane decreased at high reaction pressure.

Table 2
The performance of (Pd–Ca/SiO_2)/β-zeolite as a function of rection pressure

Catalyst	(Pd–Ca/G3)/β-zeolite				
Total pressure (MPa)	1.1	2.1	3.1	4.1	5.1
Conversion of CO (%)	25.8	41.0	62.2	65.5	71.3
Product yield (C%)					
Hydrocarbons	14.3	22.8	35.3	37.7	42.3
C3 + C4	10.4	16.8	25.9	25.9	29.4
DME	0.0	0.0	0.0	0.0	0.0
CO_2	11.4	18.2	26.9	27.8	29.0
Hydrocarbon distribution (C mol%)					
C_1	11.3	4.0	2.5	2.5	1.8
C_2	6.7	8.5	9.6	10.6	10.3
C_3	42.1	37.5	35.9	31.6	32.3
C_4	30.8	36.3	37.4	37.1	37.3
C_5	7.0	10.8	11.7	14.8	14.8
C_{6+}	2.0	2.9	2.9	3.5	3.5
C_3 + C_4	73.0	73.7	73.3	68.7	69.6

H_2/CO = 2,350 °C, W/F = 9.0 g h/mol, (Pd–Ca/SiO_2)/β-zeolite = 2/1 (by weight).

This is favorable because methane is the most unfavorable product in this process. The low CO conversion resulted in lighter hydrocarbons, this could be attributed to the cracking of long chain hydrocarbon in zeolite. So the medium reaction pressure (4.0–6.0 MPa) was suitable for the LPG synthesis from syngas using the (Pd–Ca/SiO_2)/*β*-zeolite hybrid catalyst.

3.4. Stability of hybrid catalysts

Figure 3 compares the performance of two kinds of hybrid catalyst, Cu–Zn/USY (1/1 by weight) and (Pd–Ca/G3)/*β*-zeolite (2/1 by weight; G3 is silica with specific surface area of 820 m^2/g). The hybrid catalyst Cu–Zn/USY demonstrated high activity and more than 75% selectivity for LPG at the initial stage of reaction at 335 °C and 2.1 MPa, but its CO conversion decreased about 40% after 52 h of time on stream. The hybrid catalyst (Pd–Ca/G3)/*β*-zeolite had almost the same selectivity for LPG and much higher one though conversion of CO than Cu–Zn/USY. Furthermore, it is clear that the activity of the hybrid catalyst (Pd–Ca/G3)/*β*-zeolite decreased more slowly than that of Cu–Zn/USY. Because supported palladium as methanol synthesis catalyst is more stable than that based on Cu and Zn oxides at high temperatures and high partial pressures of CO_2 and H_2O. The higher reaction temperature also decreased the yield of heavier hydrocarbons (more than 5 pentanes), which was deleterious for the activity of zeolite. On other hand, *β*-zeolite is more thermally stabe than Y-type zeolite.

3.5. X-ray diffraction (XRD)

The samples of hybrid catalyst (Pd–Ca/G3)/*β*-zeolite were examined by XRD to determine the chemical form and crystallite size. As figure 4 shows, the hybrid catalyst before reduction showed a typical peak of

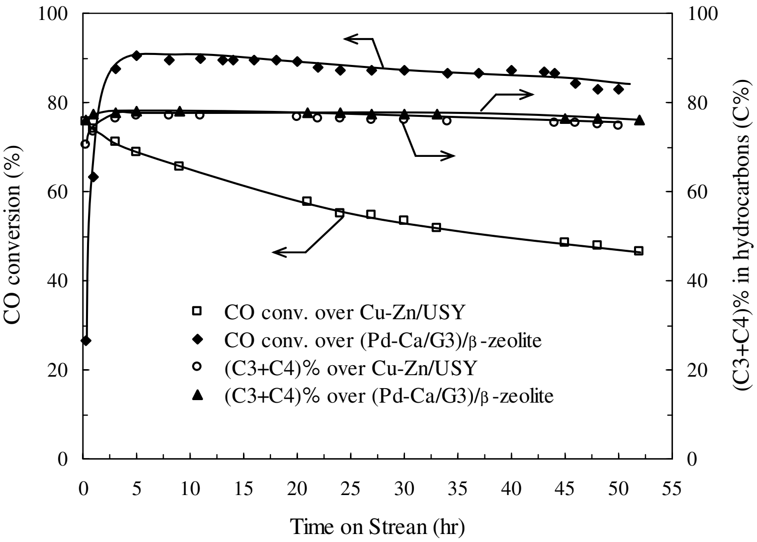

Figure 3. The performance of hybrid catalyst as a function of time on stream, (Pd–Ca/G3)/*β*-zeolite: 375 °C, 5.1 MPa, W/F = 9.0 g h/mol, (G3 is SiO_2 with a specific surface area of 820 m^2/g), Cu–Zn/USY: 335 °C, 2.1 MPa, W/F = 4.5 g h/mol.

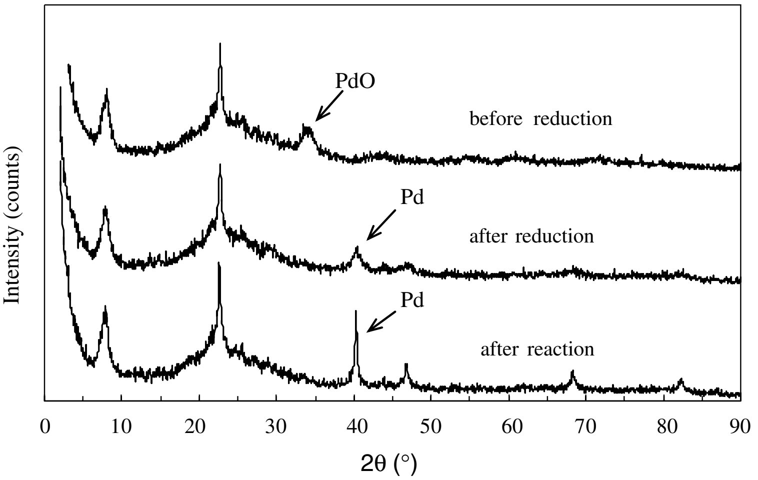

Figure 4. XRD spectra of hybrid catalysts.

PdO(101), and reduced hybrid catalyst showed a peak of metal palladium (111) [16]. That 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 (111) give the corresponding size of Pd metal, 10 and 22 nm, showed in table 3. XRD demonstrated that the crystallite size of β-zeolite did not change during the reduction and reaction. Figure 2 also indicated that the high specific surface area of supports in Ca-Pd/SiO_2 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 3
Data of XRD

Catalyst	(Pd–Ca/G3)/β-zeolite		
	Before reduction	After reduction	After reaction
Peak	PdO(101)	Pd(111)	Pd(111)
2 θ (°)	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 (Pa-Ca/G3)/β-zeolite showed higher stability and activity than Cu–Zn/USY and more than 75% selectivity for LPG fraction. This catalyst would enable the process of producing LPG from natural gas.

Acknowledgment

This project was financially supported by Japan Gas Synthesis Ltd. That is great appreciated.

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