

# Direct synthesis of LPG from synthesis gas over Pd–Zn–Cr/Pd- $\beta$ hybrid catalysts

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## Abstract

The reaction of synthesis gas to liquefied petroleum gas (LPG) over Zn–Cr-based hybrid catalysts was systematically investigated in this paper. The results show that the synergistic effect, existed in the Zn–Cr-based methanol synthesis component and  $\beta$  zeolite, results in the high performance of hybrid catalysts for synthesis gas to LPG. Active metal Pd in the  $\beta$  zeolite mainly play the role of olefin hydrogenation, which promotes the reaction of the title-mentioned overall reaction. The ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  in Pd- $\beta$  has a large influence on the stability of hybrid catalysts for syngas to LPG. As the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio increases, CO conversion slightly decreases, however, the catalytic stability of Zn–Cr-based hybrid catalysts is largely improved. The characterization results indicated that during the reaction, the decreasing of acidic sites is the main reason of catalyst deactivation.

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**Keywords:** Liquefied petroleum gas; Synthesis gas; Zn–Cr-based hybrid catalyst

## 1. Introduction

Liquefied petroleum gas (LPG), a mixture of propane and butanes, has environmentally benign characteristics and widely been used as clean fuels [1]. Direct synthesis of LPG from syngas is an important choice for converting natural gas to high-value-added products. Differently from F–T synthesis reaction mechanism [2–6] that the product hydrocarbons follow Anderson–Schulz–Florry distribution, the direct synthesis of LPG from syngas could be carried out over a hybrid catalyst composed of methanol synthesis catalyst and zeolite [7–9].

Cu–ZnO is lower temperature methanol synthesis catalyst, which is easily deactivated at high temperature (>300 °C) which is the common operation temperature for syngas to LPG [7]. Pd/SiO<sub>2</sub> methanol catalyst is expensive due to the high Pd content in the catalyst [8], Zn–Cr is reported to be a high-temperature methanol synthesis catalyst [10,11].

It is reported that ZSM-5, USY, and  $\beta$  zeolites are generally hybrid catalyst components for syngas to LPG [7–9,12,13].

Among them,  $\beta$  zeolite exhibits the best LPG selectivity. It is a common fact that the acidic properties of zeolite are strongly related to its  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and crystallization [14–20].

Therefore, the present investigation aims at the studies of low Pd content high-temperature Pd–Zn–Cr/Pd- $\beta$  hybrid catalyst, which combined Pd–Zn–Cr methanol synthesis components with modified  $\beta$  zeolite (Pd- $\beta$ ). The interaction of Pd–Zn–Cr and Pd- $\beta$ , and the effect of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio on the performance of catalysts for syngas to LPG were discussed in detail.

## 2. Experimental

### 2.1. Catalyst preparation

Pd–Zn–Cr methanol synthesis catalyst was prepared by impregnation method [11] and modified  $\beta$  zeolite is prepared by ion-exchange method [21].

The Pd–Zn–Cr methanol synthesis catalyst and modified  $\beta$  zeolite (Pd- $\beta$ ) were firstly pressure-molded, crushed and sieved to the particles of 0.36–0.71 mm, respectively. The two kinds of particles were then mechanically mixed well to form hybrid catalyst of Pd–Zn–Cr/Pd- $\beta$ .

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## 2.2. Catalytic reaction test

A pressurized flow type 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. A thermocouple was set at the axial center of the tubular reactor. Unless noted elsewhere, 1 g of hybrid catalyst was placed in the reactor with inert quartz sands above and under the catalyst. The catalyst was activated in a flow of hydrogen at 400 °C for 3 h. All the products from the reactor were introduced in gaseous state and analyzed by gas chromatography (GC) on line. CO and CO<sub>2</sub> were analyzed by a GC equipped with the thermal conductivity detector (TCD) and a column of activated charcoal, and light hydrocarbons were analyzed by another GC equipped with the flame ionization detector (FID) and a column of Porapak-Q. Argon was added in the reaction feed as an internal standard for analysis.

## 2.3. Catalyst characterization

The XRD patterns of catalyst sample were recorded by a Rigaku diffractometer (Ni-filtered Cu K $\alpha$  radiation, 50 kV, 36 mA). The NH<sub>3</sub>-TPD of catalyst sample was measured by TPDRO 1100 (ThermoQuest Corp.). The adsorption of NH<sub>3</sub> was performed at 100 °C, and the sample were subsequently purged for 1 h in a flow of helium at 100 °C, and then the TPD was carried out from 50 to 650 °C with a heating rate of 10 °C min<sup>-1</sup> under a helium flow of 30 ml min<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Catalytic performance of catalysts for the reaction of syngas to LPG

The catalytic reaction of syngas to LPG over Pd- $\beta$ , Pd-Zn-Cr, and Pd-Zn-Cr/Pd- $\beta$  catalysts was carried out at 350 °C, 5.1 MPa, W/F = 1.9 g h mol<sup>-1</sup>, H<sub>2</sub>/CO/Ar = 54/27/19, 0.2 g catalyst loading. The results were listed in Table 1. It is noted that Pd- $\beta$  and Pd-Zn-Cr have very lower activities for syngas to LPG, CO conversion is only 4.4 and 2.4%, respectively. Methanol is the main reaction product over Pd-Zn-Cr while hydrocarbons over Pd- $\beta$ . In the hydrocarbon distribution, methane and ethane are occupied more than 60%, even 97% over Pd-Zn-Cr catalyst.

For the hybrid catalyst Pd-Zn-Cr/Pd- $\beta$  exhibits a better catalytic performance for syngas to LPG, CO conversion could achieve 29.3%, and LPG selectivity in hydrocarbon ((C<sub>3</sub> + C<sub>4</sub>)/hydrocarbons) is 79.2%, which is far higher than those over Pd-Zn-Cr or Pd- $\beta$  catalysts. In addition, methane and ethane, which are the most unfavorable products in this process, have occupied only 10.5% in the hydrocarbons.

The above results indicate that the synergistic effect exists between Pd-Zn-Cr and Pd- $\beta$  components in the reaction of syngas to LPG. Pd-Zn-Cr shows a good methanol synthesis function while Pd- $\beta$  exhibit excellent dehydration of

Table 1  
The reaction performances of catalysts for syngas to LPG

	Catalyst		
	Pd- $\beta$	Pd-Zn-Cr	Pd-Zn-Cr/Pd- $\beta$
CO conversion (mol%)	4.4	2.4	29.3
Product yields (C mol%)			
CO <sub>2</sub>	0.9	0.3	15.1
CH <sub>3</sub> OH	0	1.9	0
CH <sub>3</sub> OCH <sub>3</sub>	0	0.1	0
Hydrocarbons	3.5	0.1	14.2
Hydrocarbon distribution (wt.%)			
C <sub>1</sub>	39.4	75.4	2.8
C <sub>2</sub>	21.4	21.7	7.7
C <sub>3</sub>	26.3	2.9	34.3
C <sub>4</sub>	11.4	0	44.9
C <sub>5</sub>	1.5	0	8.5
C <sub>6+</sub>	0	0	1.8
(C <sub>3</sub> + C <sub>4</sub> )/hydrocarbons (wt.%)	37.7	2.9	79.2

methanol and DME due to its acidic sites [11]. Therefore, over the Pd-Zn-Cr/Pd- $\beta$  hybrid catalyst, methanol/DME were first formed from synthesis gas over Pd-Zn-Cr and then in situ transformed to hydrocarbons (mainly propane and butane) over Pd- $\beta$ . It is just because the synergistic effect existed in the hybrid catalyst, the CO conversion of syngas to LPG is largely improved, even broke the limitation of methanol synthesis thermodynamic equilibrium at reaction conditions.

### 3.2. Effect of active metal Pd on the reaction performance of Pd-Zn-Cr/Pd- $\beta$ catalysts

To further investigate the role of active metal Pd, the hybrid catalysts containing 0.5 wt.%Pd and Pd-free hybrid catalysts for syngas to LPG were tested at 350 °C, 2.1 MPa, and Ar/H<sub>2</sub>/CO/CO<sub>2</sub> = 3/65/24/8, the results are shown in Table 2. The results show that, Pd-free catalyst showed a low activ-

Table 2  
The reaction performance of catalysts for syngas to LPG

	Catalyst	
	Zn-Cr/ $\beta$	Pd-(Zn-Cr/ $\beta$ )
CO conversion (mol%)	21.4	33.9
Product yields (C mol%)		
CO <sub>2</sub>	8.9	13.3
CH <sub>3</sub> OH	0	0
CH <sub>3</sub> OCH <sub>3</sub>	0.06	0
Hydrocarbons	12.5	20.6
Hydrocarbon distribution (wt.%)		
C <sub>1</sub>	5.0	3.8
C <sub>2</sub>	11.5	8.9
C <sub>3</sub>	45.1	48.2
C <sub>4</sub>	31.2	31.9
C <sub>5</sub>	5.4	5.4
C <sub>6+</sub>	1.8	1.6
(C <sub>3</sub> + C <sub>4</sub> )/HC	76.3	80.2

Table 3

The reaction performances of Pd–Zn–Cr/Pd- $\beta$  catalysts including different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio  $\beta$

	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> ratio (mol/mol)		
	37	243	300
CO conversion (mol%)	78.7	74.6	72.0
Product yields (C mol%)			
CO <sub>2</sub>	27.0	25.3	25.1
DME (CH <sub>3</sub> OCH <sub>3</sub> )	0.05	0.03	0.11
Hydrocarbons	51.7	49.3	46.8
Hydrocarbon distribution (wt.%)			
C <sub>1</sub>	5.2	2.4	2.3
C <sub>2</sub>	9.2	3.4	3.0
C <sub>3</sub>	52.5	39.4	37.4
C <sub>4</sub>	26.9	39.9	40.6
C <sub>5</sub>	4.7	9.0	9.7
C <sub>6+</sub>	1.5	6.0	7.0
(C <sub>3</sub> + C <sub>4</sub> )/hydrocarbons (wt.%)	79.4	79.2	78.0

ity, because Cr–Zn had low activity for methanol synthesis at 2.1 MPa. Added palladium in Cr–Zn resulted in the high activity for LPG synthesis, while keeping the LPG selectivity ((C<sub>3</sub> + C<sub>4</sub>) % in hydrocarbons) almost constant. In addition, it is noted that the LPG fractions containing amount of olefins over Pd-free catalyst while almost no olefins was found in the LPG fraction over catalyst containing Pd. This demonstrated that the small amount of Pd on Cr–Zn and  $\beta$  zeolite could catalyze olefin hydrogenation to paraffins, which will be beneficial to the activity and selectivity of hybrid catalyst for syngas to LPG.

### 3.3. Effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio on the reaction performance of Pd–Zn–Cr/Pd- $\beta$ catalysts

The acid properties of Pd- $\beta$  have an important influence on the dehydration function of Pd–Zn–Cr/Pd- $\beta$  catalyst, and simultaneously the acidic sites are related to SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of Pd- $\beta$ . So, effects of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio on hybrid catalysts were investigated at 375 °C, 5.1 MPa, W/F = 8.9 g h mol<sup>-1</sup>, H<sub>2</sub>/CO/CO<sub>2</sub> = 65/24/8, the results are listed in Table 3.

It is seen from Table 3 that with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio increasing from 37 to 300, CO conversion, hydrocarbon yield and LPG selectivity ((C<sub>3</sub> + C<sub>4</sub>)/hydrocarbons) slightly decrease from 78.7, 51.7, and 79.4 to 72.0, 46.8, and 78.0%, respectively. In hydrocarbon distribution, C<sub>1</sub>–C<sub>3</sub> hydrocarbons decrease while C<sub>4</sub>–C<sub>6</sub> hydrocarbons increase as SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of catalysts increases. This is due to the acidic sites of Pd- $\beta$ , which are mainly related to Al<sub>2</sub>O<sub>3</sub> component, decrease with increase in SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, and the dehydration ability from MeOH/DME to hydrocarbons becomes weak, and further the catalytic activity of catalysts decreases.

### 3.4. Effect of reaction temperature on the reaction performance of Pd–Zn–Cr/Pd- $\beta$ catalysts

To further investigate the interaction of Pd–Zn–Cr and Pd- $\beta$  components during reaction, the effect of reaction

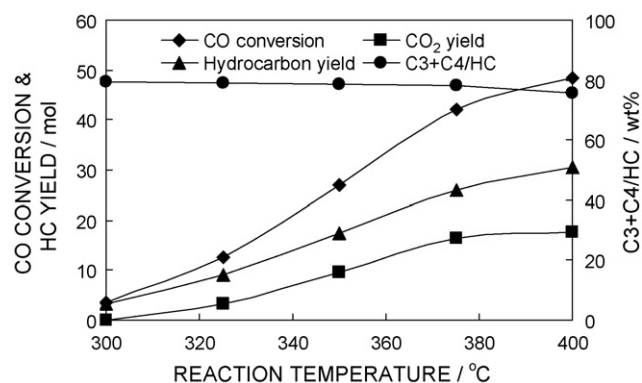


Fig. 1. Influence of reaction temperature on the reaction performance of Pd–Zn–Cr/Pd- $\beta$  catalysts.

temperature on the reaction performance of catalyst was carried out at 5.1 MPa, W/F (catalyst weight/feed gas flow rate) = 1.9 g h mol<sup>-1</sup>, H<sub>2</sub>/CO/Ar = 54/27/19, the results, obtained at reaction 1 h, were shown in Fig. 1.

It could be seen that as reaction temperature increases from 300 to 400 °C, CO conversion, hydrocarbon (HC) yield, and CO<sub>2</sub> yield evidently increase, respectively, the increasing trends become slow after 375 °C. However, LPG (C<sub>3</sub> + C<sub>4</sub>) selectivity slightly decreases.

From the product hydrocarbon distribution shown in Fig. 2, it could be learned that selectivity to C<sub>1</sub>–C<sub>3</sub> increases and selectivity to C<sub>4</sub>–C<sub>6+</sub> decreases with increase in reaction temperature. Combining the factors of conversion, LPG selectivity, and hydrocarbon distribution, it is thought that 370–400 °C is the suitable reaction temperature for LPG synthesis from syngas over Pd–Zn–Cr/Pd- $\beta$  catalyst, which is very different from that (325–350 °C) over Cu–Zn/USY catalyst [1]. In addition, largely different from Cu–Zn/USY catalysts, no DME was detected during the investigated temperature range, this is due to the low activity of Zn–Cr methanol synthesis at low temperature and high dehydration and olefin hydrogenation ability of Pd- $\beta$  at high temperature. The methanol and little amount of DME were detected in the products of syngas to LPG over Pd–Zn–Cr catalyst, which proved that the reaction of syngas to LPG is followed as the reaction routes: syngas to LPG via methanol/DME over Pd–Zn–Cr/Pd- $\beta$  catalyst.

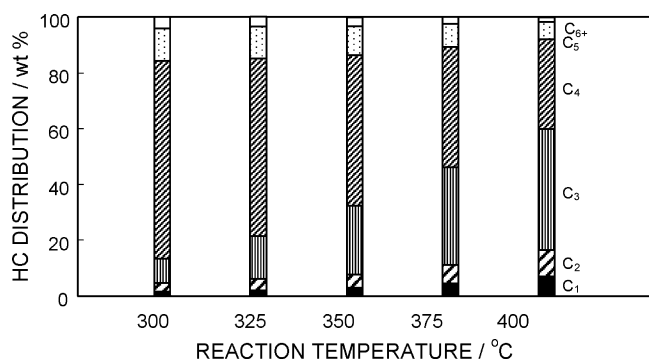


Fig. 2. Influence of reaction temperature on the product hydrocarbon distribution over Pd–Zn–Cr/Pd- $\beta$  catalysts.

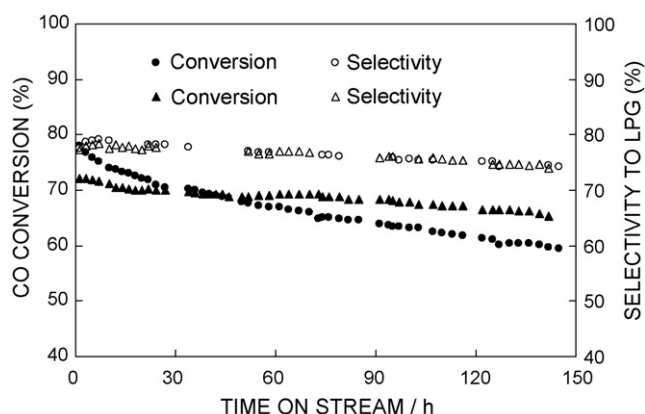


Fig. 3. Catalytic stability of Pd-Zn-Cr/Pd- $\beta$  with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in Pd- $\beta$  (○, ● 37; ▲, △ 300).

### 3.5. Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio on the stability of Pd-Zn-Cr/Pd- $\beta$ catalysts

The effects of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio on the catalytic stability of hybrid catalysts were also investigated at 375 °C, 5.1 MPa, W/F: 8.9 g h mol<sup>-1</sup>,  $\text{H}_2/\text{CO}/\text{CO}_2/\text{Ar} = 65/24/8/3$ , the results were shown in Fig. 3.

It could be learned from Fig. 3 that both catalysts have the similar LPG selectivity (>75%) during 150 h operation. The high selectivity to LPG was attributed to three dimensions structure and large pore size of  $\beta$  zeolite. Olefins (propylene and butanes) in product hydrocarbons formed in the cage of  $\beta$  zeolite would easily leave the active site and diffused to the surface of Pd for hydrogenation reaction. Hydrogenation of olefins would stop the growth of carbon chain and decrease the yield of heavy hydrocarbons and coke on the surface of catalyst. There were no olefins found in the product, because the intermediate olefins produced from methanol/DME were hydrogenated in situ catalyzed by Pd. Simultaneously, olefin hydrogenation suppressed the yield of heavy hydrocarbons.

During 150 h reaction, the catalyst with 300 of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio Pd- $\beta$  exhibit better catalytic stability, CO conversion decreases from 72.2 to 65.4% while CO conversion decreases from 78.7 to 59.4% over the catalyst with 37 of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in Pd- $\beta$ .

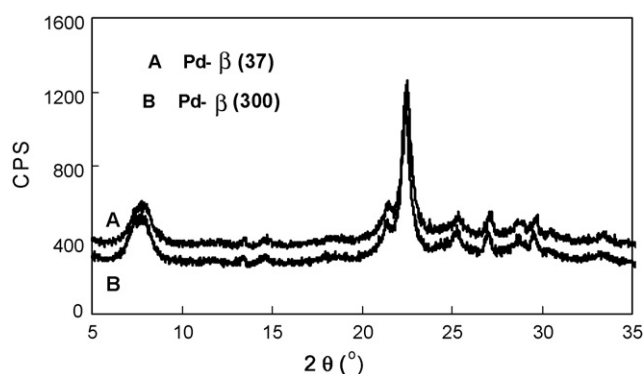


Fig. 4. XRD spectra of Pd- $\beta$  zeolites containing different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio.

Altogether, although the catalyst with 37 of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio Pd- $\beta$  exhibits a little higher catalytic activity and LPG selectivity, the catalyst with 300 of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio Pd- $\beta$  should be chosen for its evident higher catalytic stability.

### 3.6. XRD spectra and $\text{NH}_3$ -TPD profiles of Pd- $\beta$ containing different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio

To find the reason of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio influencing the reaction performance, XRD and  $\text{NH}_3$ -TPD of Pd- $\beta$  zeolites have been carried out. XRD spectra shown in Fig. 4 of Pd- $\beta$  with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio show that two kinds of Pd- $\beta$  zeolites exhibit similar XRD diffraction peaks of  $\beta$  zeolite, which indicates that Pd- $\beta$  zeolites with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio have similar tetragonal crystal  $\beta$  structure, which is corresponding to the similar catalytic performance of Pd-Zn-Cr/Pd- $\beta$  catalysts: high CO conversion (>70%) and high LPG selectivity (>78%). Thus, what cause the difference of catalytic performance of different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio catalysts is still to be solved.

$\text{NH}_3$ -TPD profiles of Pd- $\beta$  with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio are shown in Fig. 5. It is shown that two kinds of  $\beta$  zeolites have a main  $\text{NH}_3$  desorbed peak at 175 and 192 °C, respectively. Compared to Pd- $\beta_{300}$  (300 of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of  $\beta$ ), Pd- $\beta_{37}$  (300 of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of  $\beta$ ) has more strong acidic sites. Combined the reaction performance of the corresponding catalysts for syngas to LPG, it is thought that the dehydration step for the reaction of syngas to LPG mainly occurs on the strong acidic

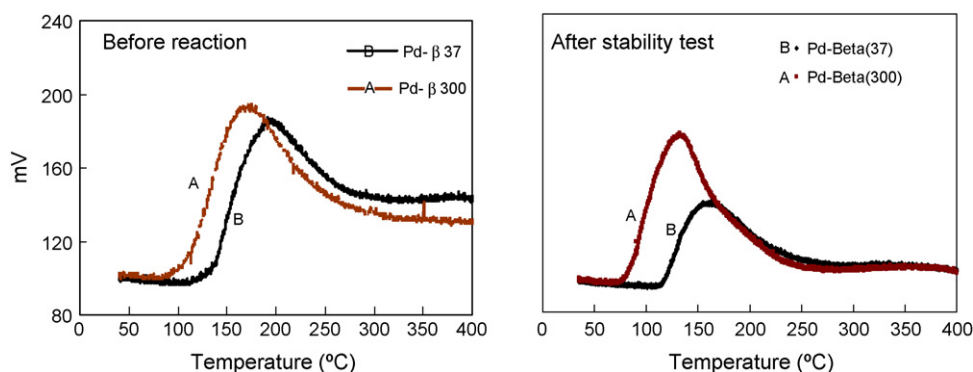


Fig. 5.  $\text{NH}_3$ -TPD profiles of Pd- $\beta$  zeolites containing different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio.

sites. These acidic sites are related to the  $\text{NH}_3$ -TPD peak temperature between 150 and 300 °C. It is noted that Pd- $\beta_{300}$  exhibits almost the same amounts of acidic sites as Pd- $\beta_{37}$ , which is different as H- $\beta$  zeolites. This may be due to the influence of ion-exchanged Pd.

In addition, the  $\text{NH}_3$ -TPD profiles of  $\beta$  zeolites after stability test indicate that the acidic sites of Pd- $\beta_{300}$  exhibit more stable than those of Pd- $\beta_{37}$ , which is consistent with the better catalytic stability of Pd-Zn-Cr/Pd- $\beta_{300}$  than that of Pd-Zn-Cr/Pd- $\beta_{37}$ . That is to say, with the ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  increasing, the amount of strong acidic sites decreases, and further decrease the activity of corresponding catalyst. However, the acidic sites of higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio Pd- $\beta$  are more stable during the reaction of syngas to LPG than those of lower  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio Pd- $\beta$  zeolites, which further keep the catalytic activity of the corresponding catalysts. Such conclusion is corresponding to the analysis results of coke formation in the catalysts after reaction, during the stability test, the coke formation over Pd-Zn-Cr/Pd- $\beta_{37}$  is much higher than those over Pd-Zn-Cr/Pd- $\beta_{300}$ . So, it is thought that the coke, formed in the reaction, will cover some acidic sites of zeolite, which result in the decrease of acidic sites, and then decrease the catalytic performance of catalyst.

#### 4. Conclusion

A synergistic effect between Pd- $\beta$  and Pd-Zn-Cr components, which largely improved the catalytic activity and selectivity of hybrid catalysts, existed in the Pd-Zn-Cr/Pd- $\beta$  hybrid catalyst for syngas to LPG. The ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of Pd- $\beta$  has a large influence on the stability of Pd-Zn-Cr/Pd- $\beta$  catalysts for syngas to LPG. As the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio increases from 37 to 300, CO conversion decreases from 78.7 to 72.2%, however, the catalytic stability of Pd-Zn-Cr/Pd- $\beta$  catalysts is largely improved. Acidic sites of Pd- $\beta$  with high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio are more stable than those of low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio Pd- $\beta$

during the reaction, which could keep the stable catalytic activity during the reaction.

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