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Full Length Article

The design of a CZ@H-β-P catalyst with core shell structure and its application in LPG synthesis from syngas

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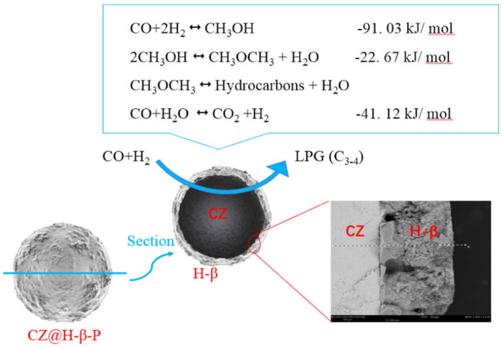
GRAPHICAL ABSTRACT



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ABSTRACT

Liquefied petroleum gas (LPG, C3 and C4 paraffins) from syngas have attracted much attention recently due to the growing demand of non-oil resource as well as its environmentally friendly features, but the catalytic reaction process controlled by thermodynamics and CO conversion rate is low with many side reactions. Here we report a catalyst with core shell structure for LPG synthesis from syngas. Zeolite as shell was synthesized by hydrothermal method firstly and then coated on Cu/ZnO core with Ludox (CZ@Z), the Cu/ZnO core was prepared by co-precipitation method. The unique core shell structure had efficient synergistic effect. The reaction equilibrium favored forward reaction because methanol as an intermediate was directly transformed to dimethyl ether. The zeolite type in the core shell structure catalyst had great effects on the activity and selectivity. The catalysts have been characterized by XRD, NH_3-TPD and SEM. The activities were determined after in situ H_2 reduction. CZ@H-β catalyst showed a more effective catalytic activity compared with the traditional hybrid catalyst. The excellent catalytic performance was attributed to the combined contribution of both unique core shell structure and proper zeolite type. At these reaction conditions, temperature of 350 °C, pressure of 3.0 MPa and flow rate of 40 ml min^{-1}, CO conversion and hydrocarbons selectivity achieved 61.8% and 64.2%, respectively. LPG selectivity in hydrocarbons was 70.2%.

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1. Introduction

Liquefied petroleum gas (LPG), an important chemical raw material and alternative clean energy, has broad application prospects [1–7]. LPG mainly comes from natural gas and oil field associated gases, crude oil refining (by-product gas) and ethylene cracking. Despite the increasing production capacity in the world, the demand for LPG is rapidly increasing as the propane dehydrogenation to propylene production project becomes more intensive. Now, there is urgent need for new technology to alleviate the growing contradiction between supply and demand [8–13]. LPG can be produced by both Fischer-Tropsch synthesis (FTS) reaction [14–17] and methanol dehydration to dimethyl ether then to hydrocarbons (MTH) process [18–20]. As a result of the reaction mechanism, the hydrocarbon products of the traditional FTS reaction process are widely distributed according to the Anderson-Schulz-Florry distribution model. The products separation difficulty leads to expensive separation casts. LPG direct synthesis from syngas using this reaction route has received significant attention during the past decade [21–25] because the route broke the Anderson-Schulz-Florry rules and the production of less by-products improved LPG selectivity [26–29]. The combined traditional methanol synthesis hybrid catalyst and zeolite promoted higher LPG synthesis from syngas, but random feed gas contact with different catalysts greatly reduced LPG selectivity and yield. LPG was synthesized by methanol production first, followed by dehydration to hydrocarbons over a two-bed reaction. However, it is difficult to accurately control the reaction steps of the simple physical mix structure of the tandem catalyst. The present paper found a special core shell structure capsule catalyst with Cu/ZnO as the core enwrapped by a zeolite shell which could provide a tailor made confined reaction environment to control the reaction step [30–34]. Compared with the traditional mechanical hybrid catalysts, this reaction route gave rise to a satisfactory selectivity for desired products. The synthesis process of LPG is involved in methanol synthesis firstly from syngas (1), methanol dehydrates to dimethyl ether (2), dimethyl ether converts into hydrocarbons (3) and the water-gas shift (WGS) reaction.

$$CO + 2H_2 \leftrightarrow CH_3OH \quad -91.03\ \text{kJ/mol} \tag{1}$$

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad -22.67\ \text{kJ/mol} \tag{2}$$

$$CH_3OCH_3 \leftrightarrow \text{Hydrocarbons} + H_2O \tag{3}$$

$$CO + H_2\ O \leftrightarrow CO_2 + H_2 \quad -41.12\ \text{kJ/mol} \tag{4}$$

$$\text{Total equation:} CO + H_2 \rightarrow CO_2 + \text{Hydrocarbons}$$

CO and H_2 were raw material gas, and H_2O comes from the Eqs. (2) and (3). Eq. (4) was the WGS reaction, Cu/ZnO core catalyst promoted Eq. (4) and carbon dioxide was produced as by-product. The methanol synthesis on the Cu/ZnO catalyst (1) is the key step in constrained by the thermodynamic equilibrium. Dimethyl ether is generated by methanol dehydrated (2) over on acidic sites of zeolite layer. The thermodynamic equilibrium of methanol synthesis process will be broken by methanol dehydration and promote Eq. (1) and suitable catalyst structure can improve CO conversion.

It is worth noting that in Eq. (3) dimethyl ether dehydrated firstly to produce the light olefins and then hydrogenated to produce paraffins. The special structure of the core shell catalyst, the high mass proportion of Cu/ZnO in the catalyst and the strong hydrogenation ability of Cu/ZnO catalyst made the olefin can be easily hydrogenated to produce paraffin [10,27].

2. Experimental

2.1. Catalyst preparation

2.1.1. Cu/ZnO and zeolite catalysts preparation

Cu/ZnO catalysts were prepared by co-precipitation method. 14.28 g copper nitrate ($Cu(NO_3)_2$) and 17.58 g zinc nitrate ($Zn(NO_3)_2$) with Cu/Zn ratio of 1:1 were dissolve in 300 ml deionized water and 28.10 g sodium carbonate ($NaCO_3$) was dissolve in another 300 ml deionized water. Then the two recipes were added into 300 ml deionized water with stirred constantly. The co-precipitation process maintained pH of 8.5 and temperature of 333 K. After standing 12 h the precipitation solution was filtered to neutral then dried at 393 K for 12 h. Finally, the dried catalyst was screened into 20–40 mesh.

2.1.2. Zeolite capsule catalyst preparation

The zeolites (H-Y, H-MOR and H-ZSM-5) were prepared for comparison by hydrothermal synthesis method [35–37]. The molar ratio of 96.53 SiO_2: 34.55 TEAOH: 1.0 Al_2O_3: 1130 H_2O: 0.00148 KNO_3 was used to hydrothermal synthesis of β zeolite. The TPAOH (tetrapropylammonium hydroxide, 25% in water) as structure directed reagent, TEOS (tetraethyl orthosilicate, 95%) as silica resource, aluminium isopropoxide (99.9%) as aluminum resource, dehydrated ethanol (99.5%) and nitric acid (69%), were purchased from Aladdin Company. The appropriate ingredients for different zeolites were sealed in autoclaves and underwent hydrothermal synthesis process then filtration and finally drying. Then β zeolite and MOR zeolite were ion-exchanged with 1 M ammonium nitrate (NH_4NO_3) to obtain H type zeolite. Before zeolite coating, Cu/ZnO core catalyst was impregnated with an adhesive of Ludox (silica sol, 40%), then added to zeolite powder in a round bottom flask for shacking. Capsule catalyst was obtained, with a uniform zeolite layer coating on Cu/ZnO core. Here the weight ratio of Cu/ZnO to zeolite was 1 to 1. The samples were dried at 393 K for 12 h and calcined at 773 K for 3 h then named as "CZ@zeolite-P" (where "P" stands for physical adhesive method). A series of CZ@zeolite-P-x were prepared by this method ("x" means the weight ratio of Cu/ZnO to zeolite).

2.1.3. Hybrid catalyst preparation

The hybrid catalyst was prepared by mixing Cu/ZnO and zeolite powder at a 1/1 Cu/ZnO to zeolite weight ratio. The mixed catalyst was granulated to 20–40 mesh and calcined at 773 K in air for 5 h. This catalyst was named as "Mix-CZ-zeolite" (where "Mix" means mechanical mixture of Cu/ZnO with zeolite).

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku RINT 2400 X-ray diffractometer with a monochromatic Cu Kα radiation, scanning 2θ from 10 to 80° at 40 kV and 40 mA·NH_3 temperature programmed desorption (NH_3-TPD) was performed on BELCAT-B3 apparatus. 0.03 g sample was placed in a quartz tube and pretreated at 573 K for 1 h then cooled down to 373 K under H_2 flow. After switching to 10 vol% NH_3 in H_3 with 30 $ml{\cdot}min^{-1}$ for 1 h, the catalyst was purged by He with 30 $ml{\cdot}min^{-1}$ for 1 h to remove physically adsorbed NH_3. Then the sample was heated from 373 K to 923 K. The released NH_3 was detected by a TCD. The surface and section morphology of catalysts were observed with a scanning electron microscope (SEM, JEOL JSM-6360LV). The elemental composition of catalysts was analyzed by an energy dispersive spectrometer (EDS, JED 2300) equipped on the SEM apparatus.

2.3. Catalytic activity tests

The catalytic activity reactions were conducted with a stainless-steel reactor (9 mm OD). 0.6 g catalyst was loaded into the reactor and fixed with quartz wool. Prior to feeding syngas the catalyst was reduced by 5 vol% H_2 in N_2 through the reactor at 220 °C with atmospheric pressure for 2 h. After that, reactant gas H_2: CO = 2:1 was used to test the catalytic activity under 3.0 MPa for 6 h with a flow rate of 40 $ml{\cdot}min^{-1}$.

All the products were analyzed on line by two gas chromatographs. One equipped with a thermal conductivity detector (TCD), in which