



Direct syngas conversion to liquefied petroleum gas: Importance of a multifunctional metal-zeolite interface



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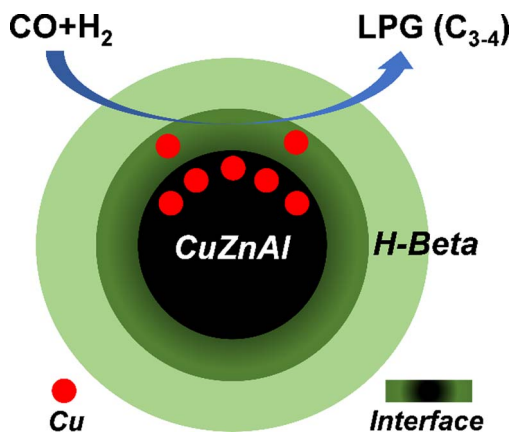
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HIGHLIGHTS

- A CuZnAl@H-Beta catalyst with a well-defined metal-zeolite interface was fabricated.
- We realized an efficient and tandem conversion of syngas to LPG.
- The LPG selectivity of in hydrocarbons reaches as high as 77%.
- A record low methane and C₂ selectivity is achieved (< 2.0%).

GRAPHICAL ABSTRACT



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ABSTRACT

It is challenging to fabricate a multifunctional catalyst for consecutively catalyzing multiple reactions. Herein, we report a well-defined metal-zeolite interface derived from a CuZnAl@H-Beta core@shell catalyst to realize one-step syngas conversion to liquefied petroleum gas (LPG). The multifunctional interface between CuZnAl core and H-Beta zeolite shell is composed of Cu and acid zeolite with a content gradient, through which synthesized methanol via syngas on the core will pass. The interface is able to catalyze the tandem dehydration of methanol to olefins on acid sites and olefin hydrogenation to C_{3–4} saturated hydrocarbons (LPG fraction) over exposed Cu sites on the interface instead of noble metals in conventional catalysts. The selectivity of LPG in hydrocarbons over the prepared capsule catalyst reaches as high as 77% accompanied by a record low methane and C₂ selectivity (< 2.0%).

1. Introduction

The increasing energy demands worldwide expedite the quest for

alternative energy sources, especially clean liquid fuels. Conversion of syngas (CO and H₂) derived from coal, natural gas, waste and biomass to hydrocarbons is a well candidate for production of valuable

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chemicals and fuels [1–4]. This process is well-known as Fischer–Tropsch (F-T) synthesis, which is successfully commercialized for decades. The high temperature F-T technology applied by Sasol process in South Africa is the largest commercial scale application with the mature Sasol Advanced Synthol (SAS) technology [5,6]. However, the conventional F-T synthesis, generally follows the Anderson–Schulz–Flory distribution law, producing a very wide range of olefins, paraffins and oxygenated compounds [7–9]. It is challenging to control hydrocarbon selectivity with certain narrow carbon number range.

Liquefied petroleum gas (LPG), a mixture of propane and butanes isomers, which is generally derived from refineries, is regarded as an environmentally benign and high-combustion value fuel due to its low carbon/hydrogen ratio, no toxicity, no corrosive activity and no aromatic hydrocarbons compared to traditional fuels [10–12]. It can be widely employed as a clean fuel, chemical feed and a propellant for aerosols. The primary driving force to the LPG application remains its low price for the end user, low pollutant emissions (especially carbon dioxide), will probably increase the interests in LPG as an internal combustion engine fuel. Nowadays, there are continuously increasing stock production of dual-fuel (gasoline–LPG) passenger car models. To date, LPG engines has been commercially available in the EU and Asian countries for many years [13]. The LPG available for the automotive market comply with a standard that does not define compositions, but limits fuel properties only [10].

There are following pathways for LPG synthesis: (1) direct synthesis from syngas; (2) indirect or semi-indirect synthesis from syngas via multiple stage reactors, including synthesis of methanol or DME from syngas and conversion of methanol or DME into hydrocarbons of LPG fraction [14,15]. From the viewpoint of energy production, the direct route of LPG synthesis from syngas is more potential and advantageous to large-scale application if compared to the indirect or semi-indirect synthesis, owing to its low energy cost, low investment scale and facile heating recycle of tail gas.

However, it is very challenging for direct synthesis of LPG from syngas over one multiple functional catalyst comprising various catalytically active sites, such as methanol synthesis, methanol dehydration to DME, DME dehydration to olefins, and olefin hydrogenation to saturated hydrocarbons. For constructing such multiple functional catalysts, a general strategy is physical mixing methanol synthesis catalyst (such as Cu/ZnO/Al₂O₃) and a noble metal-modified zeolite for a hybrid catalyst [16–19]. Both of the Cu/ZnO/Al₂O₃ and zeolite catalysts have been commercially applied. The former is the most commonly employed catalysts for methanol synthesis in industry [20]. The latter is successfully served in the field of large-scale separation and purification and catalytic dehydration process [21]. Unfortunately, it is difficult to control distribution of active sites over these hybrid catalysts. The catalytic performance is easily influenced by the contact state between various hybrid components.

In recent years, the spherical zeolite capsule structure with metal-based catalyst as core and zeolite layer as shell is been widely reported as efficient catalysts in tandem catalytic reactions, such as syngas to isoparaffins [22], syngas to DME [23,24], glycerol conversion to 1,2-PDO and 1,3-PDO [25]. However, in above cases, only typical tandem reactions including two steps are realized. There are no reports concerning the possibility of three or more catalytic tandem reactions over zeolite capsule catalysts.

Herein, we report one-step controlled tandem catalytic production of LPG from syngas achieved by a core–shell capsule catalyst CZA@β comprising Cu/ZnO/Al₂O₃ as core and H-Beta zeolite as shell. The interface with controlled gradient of Cu and zeolite between two components is key to the tandem process of three or more catalytic reactions. The advantages of core–shell catalyst prepared with the hydrothermal method is demonstrated by comparing with physical mixed catalyst Mix-CZA-β and physically prepared core–shell catalyst CZA@β-P in detail. In addition, obvious economy and social value will be produced in the real application of direct conversion of syngas to

LPG from the estimation of production in a pilot-scale plant.

2. Experimental section

2.1. Catalyst preparation

The Cu/ZnO/Al₂O₃ (CZA) catalysts were prepared by coprecipitation method. The Al(NO₃)₃·9H₂O (2.49 g), Cu(NO₃)₂·3H₂O (7.139 g) and Zn(NO₃)₂·6H₂O (8.790 g) was added into 300 mL deionized water, then the aqueous solution and Na₂(CO₃) solution (0.5 M) were dropwise (3 mL min⁻¹) into another 300 mL deionized water with pH and temperature of 8.0 and 60 °C, respectively. After aged for 12 h, the obtained slurry was washed with deionized water for several times to remove the excessive sodium ions, and subsequently, dried for 12 h, calcined at 350 °C for 2 h and pelletized to 20–40 mesh, this CZA as the core catalyst.

The template agent TEOAH (Tetraethyl ammonium hydroxide, 25% in water), fumed silica (99.5%), aluminium isopropoxide (99.0%), potassium nitrate (99.0%) and dehydrated ethanol (99.5%) were purchased from Aladdin Co. The zeolite synthesis recipe with molar ratio of 96.53 SiO₂:34.55 TEOAH:1.0 Al₂O₃:1130 H₂O:0.00148 KNO₃ was used to hydrothermal synthesis of β zeolite. This slurry stirred for 6 h at room temperature in a Teflon container, which is defined as the mother liquid of H-β zeolite. Then it is moved the Teflon container into homogeneous reactor for hydrothermal synthesis with the rotation rate of 2 rpm at 155 °C for 72 h. The final samples were separated from the slurry and ion-exchanged with 100 mL ammonium nitrate (0.5 M) for 10 h at 50 °C, dried at 120 °C for 12 h and calcined at 550 °C for 5 h to remove the organic template, H-β zeolite was obtained.

The mother liquid of H-β zeolite was used to prepare H-β zeolite shell on CZA core. After this slurry stirred for 6 h at room temperature in a Teflon container, CZA core was added into the slurry and repeated the zeolite hydrothermal synthesis, drying and calcination steps, the catalyst obtained by this process was named “CZA@β”.

Another CZA core catalyst was impregnated in silica sol (Ludox), then the wetted CZA catalyst was moved into a crucible with appropriate amount of H-β zeolite powder. The catalyst obtained after strong swaying was named “CZA@β-P”.

The physical mixed catalyst Mix-CZA-β is prepared by mixing CZA and H-β zeolite powders with a mortar.

All the catalysts are pelletized to 20–40 mesh. All the weight ratio of CZA to H-β zeolite for CZA@β, CZA@β-P, Mix-CZA-β is controlled as the same value of 10:1.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded using a D8 ADVANCE diffractometer with Cu-Kα radiation (40 kV, 40 mA) as the X-ray source.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis were carried out using JSM-6360LV scanning electron microscope with 15 kV accelerating voltage.

NH₃ temperature-programmed desorption (NH₃-TPD) measurements were performed on BELCAT-B3 instrument. Typically, 30 mg sample was pretreated in a quartz reactor with He flow at 300 °C for 1 h, then sample was cooled down to 373 K and switched the gas to NH₃-He (10 vol% NH₃) for 1 h. Sample was flushed using He of 30 mL min⁻¹ to remove the gas phase NH₃. The NH₃-TPD experiment was performed in He flow of 30 mL min⁻¹ by increasing the temperature from 100 °C to 650 °C at a heating rate of 10 K min⁻¹, the desorbed NH₃ was detected by a thermal conductivity detector (TCD).

The specific surface areas of catalyst were measured by N₂ physical adsorption experiments by Quantachrome Autosorb-IQ-C at -196 °C. The sample was outgassed at 200 °C for 1 h before N₂ physisorption. Surface area and pore size were calculated by BET and BJH method, respectively.

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