Catalysis
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Catalysis Science & Technology

Direct Synthesis of LPG from Syngas in Slurry Phase

Qianwen Zhang[a]*, Ting Ma[b], Ming Zhao[a], Teppei Tomonobu[b] and Xiaohong Li[b]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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An original catalytic system of light hydrocarbon synthesis from syngas over a hybrid catalyst in the slurry phase was investigated. N-cetane as the solvent remarkably increased the stability and activity of the catalyst by efficient removal of reaction heat. The synthesis of light hydrocarbons in a slurry phase reaction requires the close contact of two components in hybrid catalyst which is different from a gas phase reaction in a fixed bed. The replacement of Cu for Pd on modification of β-zeolite increased the activity and stability of the catalyst and the selectivity of LPG by removing water from the zeolite. The effect of the Cu content on the performance of the process was systemically studied.

1. Introduction

In the recent years, many research studies [1-9] focused on the synthesis of light hydrocarbons from coal, natural gas or biomass through syngas as an intermediate due to the rising price of fuel and less dependency on crude oil. The syngas which is produced by reforming natural gas or the gasification of coal or biomass is an important intermediate for synthesizing fuel. This approach provides an alternate route for exploitation of the huge quantities of coal, natural gas and biomass for production of clean fuel.

As Fig. 1 shows, various options are available for production of light hydrocarbons from syngas. They are: (1) Fisher-Tropsch (F-T) synthesis, (2) direct conversion of syngas by modified F-T synthesis, (3) indirect conversion of syngas by methanol or DME, (4) direct conversion of syngas over a hybrid catalyst consisting of a zeolite and methanol synthesis catalyst.
Liquefied petroleum gas (LPG), a mixture of propane and butanes, has many advantages with respect to other synfuels: it has environmentally benign characteristics used as a clean fuel and a propellant for aerosols, it is easily convertible chemical feedstock, it conveniently be stored and transported as a liquid phase, it can count on a high social acceptance for substitution for gasoline and natural gas.

The hybrid catalyst which consists of methanol synthesis catalyst and zeolites has been developed for direct synthesis of LPG from syngas in fixed bed reactor through an intermediate of methanol or DME [9-13]. These reactions usually take place in a gas phase. A gas phase reaction will result in a high temperature rise with high CO conversion due to the intense exothermic reaction of methanol synthesis from syngas. However, due to the limitation of a fixed bed reactor, the reaction heat cannot be removed efficiently from the reactor. Thus, a hotspot will emerges in the catalyst bed and consequently result in the quick deactivation of the catalyst by sintering.

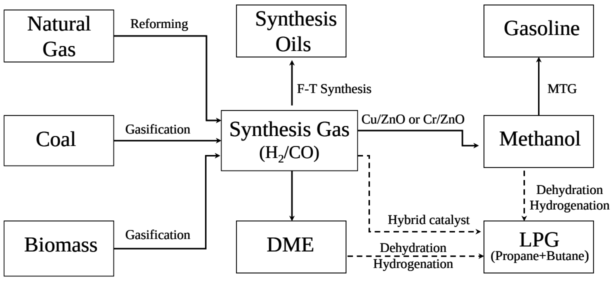

Fig. 1 Hydrocarbon synthesis process diagram

In order to avoid the appearance of the hotspot in fixed bed reactor, supercritical fluid (SCF) or near critical technology has been attempted in Fischer–Tropsch synthesis and showed better performance than the fixed bed reactor because of the better heat transfer properties[14-18]. In one of our previous reports, the selective synthesis of light hydrocarbons from synthesis gas was performed in near-critical phase. The introduction of near critical fluid not only increased the stability of the catalysts, but also increased the selectivity of light hydrocarbons and remarkably decreased the yield of CO_2[19].

Many investigations have demonstrated the advantages of a slurry reactor for the gas-to-liquid process [20-22]. Compared to a fixed bed reaction system, the slurry bed reaction system has better mixing characteristics and provides easier control of the reaction temperature. Also, the product of light hydrocarbons will easily be separated from liquid solvent because of big difference of boiling points between the product and solvent.

In the present research, the selective synthesis of LPG from syngas was performed in the slurry phase with the hybrid catalyst based on a Cu-Zn methanol synthesis catalyst and modified β-zeolite. The results show that the slurry reaction system has

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[a] *Faculty of Materials and Chemical Engineering, Beijing Institute of Petrochemical Technology, Qingyuanbeilu 14, Huangcun, Daxing District, Beijing 102617, P.R. China.*
[b] *Faculty of Environmental Engineering, the University of Kitakyushu, 1-1, Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka, 808-0135, Japan.*
**Corresponding author. Tel.: +86 10 81292750; fax: +86 10 81292750*
E-mail address: zhangqianwen@bipt.edu.cn (Q. Zhang).

† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

promising applications in the direct synthesis of light hydrocarbons from syngas.

2. Experimental

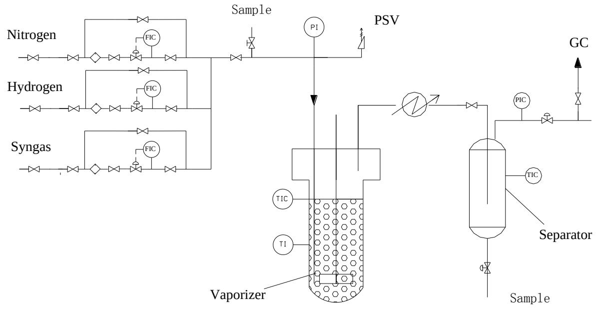
2.1. Catalyst preparation

The hybrid catalyst employed in this study consisted of a Cu-Zn oxide based methanol synthesis catalyst and a modified β-zeolite. The Cu-Zn oxide based methanol synthesis catalyst was a commercial catalyst of MK-121 with specific area of 85.2 m^2/g (BET) supplied by TOPSOE. The β-zeolites with silica to alumina ratio of 300 (BET specific area of 385.5 m^2/g supplied by TOSO) were first pretreated to become proton-type. These β-zeolites were modified with Pd by ion exchange in the ammonia solution of palladium chloride, and with Cu by incipient wetness impregnation in the water solution of $Cu(NO_3)_2$.

The hybrid catalyst was prepared by physical mixing of required amount of methanol catalyst and the zeolite. They were ground together, mixed finely, pressed, crushed, and then sieved to particles with a size of 20/40 mesh (0.35~0.71mm).

2.2. Apparatus and procedures

The reaction was carried out in a stainless steel autoclave. The experimental set-up scheme is shown in Fig. 2. The apparatus was equipped with a temperature controller for a furnace, a stainless steel autoclave with a volume of 100 ml, thermal mass flow controllers for gas flows and a back-pressure regulator; 50 ml of liquid solvent (n-cetane) and 5g of hybrid catalyst were placed into the reactor. Before the reaction, the catalyst was reduced in 5 % H_2 in N_2 at 300 ℃ for 8 h. The weight ratio of the methanol synthesis catalyst to the modified zeolite is 1:4.



Note:
FIC, flow indicator and controller: PIC, pressure indicator and controller:
TIC, temperature indicator and controller, PI, pressure indicator;
TI, temperature indicator; GC, gas chromatograph.

Fig. 2 Experimental set-up scheme

A mixture of H_2 and CO with a H_2/CO molar ratio of 2 was used as the syngas reactant. The operating conditions were T = 280 ℃, P = 3.5 MPa, W/F (syngas) = 23 g·h mol^{-1}, and the stirring speed was maintained at 1050 rpm.

All products from the reactor were sampled in a gaseous state and analyzed by gas chromatography (GC) online. CO, CO_2 and CH_4 were analyzed by a GC equipped with a thermal conductivity detector (TCD) and a column of activated charcoal. Light hydrocarbons were analyzed by another GC equipped with a flame ionization detector (FID) and a capillary column of Porapak-Q. Argon was added to the reaction feed as an internal standard for analysis.

2.3. Measurement of hydrogen chemisorption

The metal dispersion in the catalysts was estimated by the hydrogen chemisorption on the metal. The uptake of the hydrogen chemisorption was measured by a hydrogen chemisorption isotherm on an Autosorb-1-C Adsorption Instrument (produced by Quantachrome Instruments Corporation). Procedures for the hydrogen chemisorption are as follows: (1) evacuation of the catalyst sample at 25 ℃ for 30 min to remove air; (2) evacuation of the catalyst sample at 25 ℃ for 90 min to remove water; (3) reduction in flowing hydrogen (30 ml min^{-1}) while heating with temperature programming (10 ℃ min^{-1}) to 400 ℃ and holding at 400 ℃ for 1 h; (4) evacuation for 1 h at 400 ℃ to remove the gas phase and adsorbed hydrogen followed by cooling in vacuum to 50 ℃; and (5) the measurement of the hydrogen uptake.

2.4. Temperature programmed desorption (TPD) of NH_3

The acid strength and the amount of zeolite were estimated through NH_3 TPD on a ChemBET TPR/TPD Chemisorption Analyzer (Quantachrom Instruments Corporation). The zeolite sample was reduced by 5 % H_2 in N_2 before the NH_3 TPD characterization. The sample chamber containing 0.5 g of modified zeolite was heated to 150 ℃ in helium for 3 h and then cooled down to 50 ℃; the reduced gas was introduced and allowed to flow through the chamber. The sample was heated from 50 ℃ to 300 ℃ at a rate of 10 ℃ min^{-1}. After holding at 300 ℃ for 90 min, the sample chamber was cooled by air to 100 ℃; ammonia flowed through the sample chamber at 30 ml min^{-1} for 60 min, and helium was switched to the sample chamber. The tail gas was connected to a TCD monitor. When the monitor signal stabilized, the temperature-programmed heating process was repeated from 100 ℃ to 600 ℃ at a rate of 10 ℃ min^{-1}. The TCD monitored the change in the flow gas through the catalysts and integrator with two pens which recorded the sample chamber temperature signals and the flow gas changes.

2.5. X-ray diffraction (XRD)

The samples of 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 light hydrocarbon synthesis from syngas over hybrid catalyst composed of methanol catalyst and zeolite is different from the F-T reaction, because methanol is an intermediate in this process. The hybrid catalyst has two functions; i.e., methanol synthesis from syngas and methanol conversion into hydrocarbons. As shown in Fig. 3, in this hybrid catalyst system, methanol formed from syngas over a methanol synthesis catalyst was converted over zeolite into DME and then hydrocarbons. Considerable amounts of CO_2 were produced with the formation of DME and hydrocarbons due to the water-gas shift reaction.

The total reaction is as following:

$$CO + H_2 \longrightarrow C_nH_{2n} + C_nH_{2n+2} + H_2O + CO_2$$

$$(n = 1, 2, \ldots, 6)$$

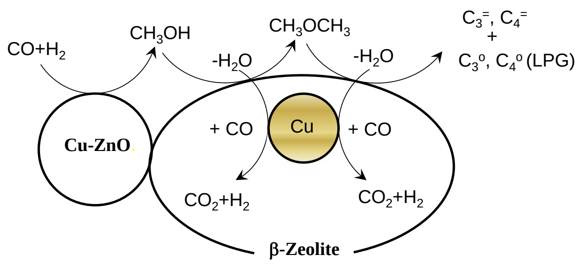


Fig. 3 Reaction mechanism of LPG synthesis from syngas

Due to the synergetic effect of methanol synthesis catalyst and zeolite, the yield hydrocarbons and one through CO conversion could reach a high level at high temperatures and low reaction pressures. The hydrocarbons in this reaction system could be paraffins, olefins and aromatic hydrocarbons. However, Cu and Pd in the hybrid catalyst are also a hydrogenation catalyst at high temperatures, so no olefins were thus detected in the reactor outlet. The aim of the present work is the selective synthesis of light hydrocarbons from syngas, especially LPG; the hydrocarbons are C_3 and C_4 paraffins.

Slurry reactors have many advantages over fixed bed reactors in a gas phase reaction for direct synthesis of hydrocarbons from syngas, including simpler construction, lower cost, excellent temperature control, lower pressure drops and the capability for the online addition and removal of a catalyst. The reaction of syngas synthesis in the gas phase over a catalyst is inevitably accompanied by the local overheating of the catalyst surface which may lead to the deactivation of the catalyst and also to an increase in the methane selectivity. This deactivation of the catalyst can be mitigated by using a slurry reactor for better heat and mass transfer, which consequently prolongs the catalyst longevity.

3.1. Performance of hybrid catalysts (Cu-Zn/Pd-β) in the slurry phase

The synthesis of light hydrocarbons in a slurry phase reaction requires the close contact of two components in hybrid catalyst which is different from a gas phase reaction in a fixed bed. Fig. 4 shows the performance of the hybrid catalyst based on a Cu-Zn oxide and a 0.5 %(wt) Pd -β-zeolite in a slurry phase reaction. CO conversion was 60.8% with a reaction time of 1 h which decreased slowly with time on stream and became constant after 4 h. Also, a considerable amount (more than 15% in yield) of DME was found in the products.

In a slurry reactor, a solid catalyst is suspended in an inert hydrocarbon liquid. Additional mass transfer resistance is existed (syngas must transfer through the slurry liquid to contact with the catalyst, and products must transfer through the slurry liquid to leave the catalyst). Experimental results demonstrate that water in the zeolite would impair the zeolite activity in converting methanol to hydrocarbons. When no water was present at the beginning of the reaction, the catalyst had high activity. The activity decreased with water increase which generated in the reaction and remained constant when the concentration of water was invariable.

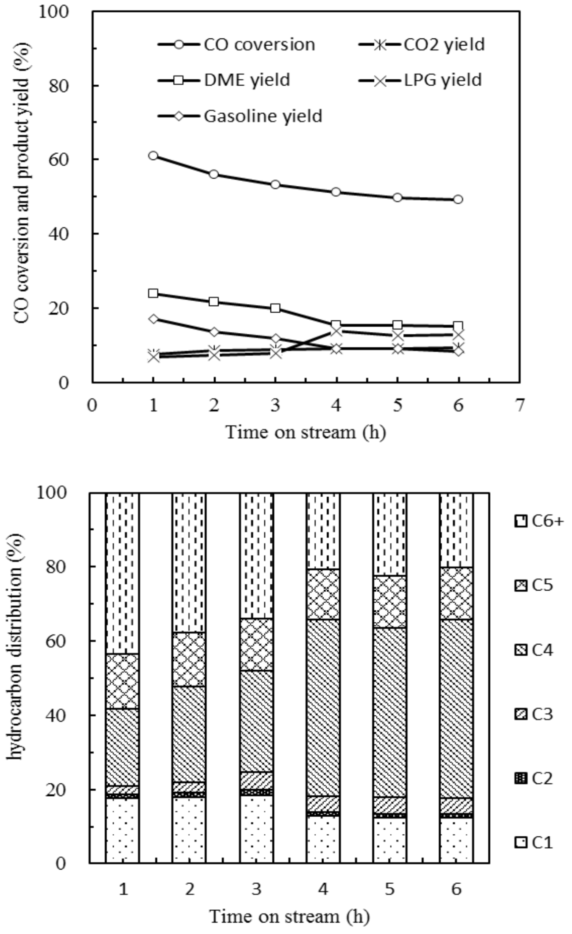


Fig. 4 Performance of hybrid catalysts (Cu-Zn/Pd-β) in a slurry phase

3.5 MPa, 280 ℃, $H_2/CO=2$, flow of syngas=80ml/min, (Cu-Zn)/0.5%(wt)Pd-β= 1/4 (by weight)

The activity of the hybrid catalyst based on Cu-Zn and Pd-β was very low when two catalyst components had loose contact where a methanol catalyst and a zeolite were shaped into particles with a size of 20/40 mesh (individually at first) and then mixed finely according to the weight ratio determined experimentally before loading into the reactor. In the slurry phase, a hybrid catalyst prepared by the above method had a CO conversion of less than 15% which is different from the gas phase and the near-critical phase [11, 19]. Due to mass transfer resistance, the methanol formed from a methanol synthesis catalyst could not be converted into DME and then to hydrocarbons over a zeolite. In the absence of a synergetic effect from a methanol synthesis catalyst and zeolite, the methanol formation equilibrium could not reach a high level at high temperatures and low reaction pressures.

3.2. Effect of copper on the performance of hybrid catalysts

1.4 %(wt)Cu was supported on a Pd modified β-zeolite by the incipient wetness impregnation method. The modified β-zeolite containing a Pd of 0.5 %(wt) was sequentially impregnated with aqueous solution of $Cu(NO_3)_2$, dried at 120 ℃ for 12 h and calcined at 350 ℃ for 4 h. The modified β-zeolite containing Pd and Cu was used in a hydrocarbon reaction synthesis from syngas with a methanol synthesis catalyst based on a Cu-Zn oxide. Fig. 5 shows the reaction performance in a hydrocarbon synthesis from syngas. Copper obviously promoted the activity and stability of the hybrid catalyst in the LPG synthesis from syngas. The addition of copper into zeolite restrained water formation and shortened residence time of water in the zeolite by the conversion of water to H_2 through a water-gas shift reaction which is confirmed by yields of CO_2. Copper has a high catalytic activity in a water-gas shift reaction. The removal of water promoted the activity and stability of the hybrid catalyst.

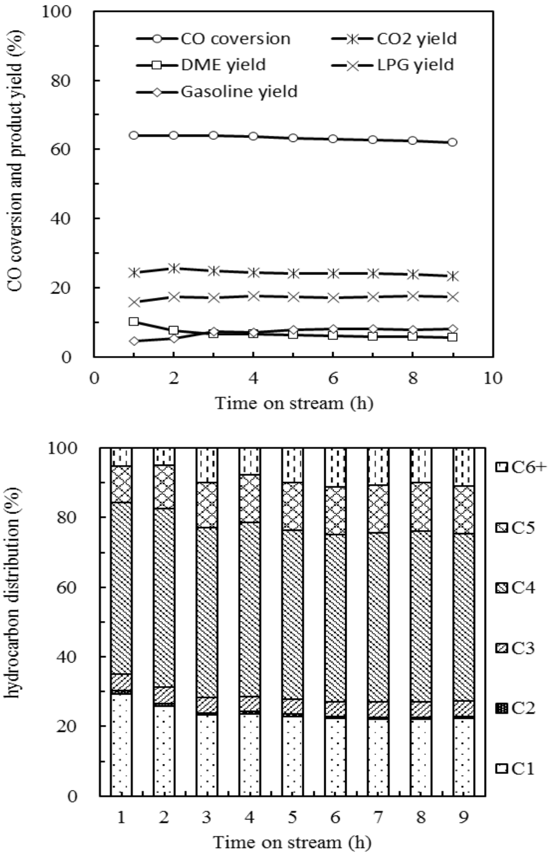


Fig. 5 Performances of hybrid catalysts (Cu-Zn/Cu-Pd-β) in a slurry phase

3.5 MPa, 280 ℃, H2/CO=2, flow of syngas=80ml/min, (Cu-Zn)/0.5%(wt)Pd-1.4%(wt)Cu-β = 1/4 (by weight)

Usually H_2 is dissociatively adsorbed on a metal surface. At room temperature, palladium is able to adsorb large quantities of hydrogen atoms after the dissociative adsorption of a hydrogen molecule. Hydrogen adsorbed on dispersed palladium or palladium block has two phases: surface hydrogen (adsorption hydrogen) and bulk hydrogen (absorption hydrogen) [23]. Tab. 1 lists data for hydrogen adsorption on catalysts.

The addition of copper to a Pd-β-zeolite resulted in a significant increase in the hydrogen adsorption volume which was favored by the hydrogenation of CO into methane[24] and explains the higher selectivity of methane in a hydrocarbon synthesis over a Cu-Zn/0.5 %(wt) Pd-1.4 %(wt) Cu-β catalyst; Copper had a weak hydrogenation adsorption. A hybrid catalyst based on a copper modified β-zeolite would have low methane selectivity in products.

Tab. 1 Hydrogen adsorption data

Catalysts	metal content % (wt)	H_2 adsorption μmol/g	active metal surface m^2/g
Pd-β-Zeolite	0.5	4.94	0.47
Pd-Cu-β-Zeolite	Pd 0.5; Cu 1.4	13.34	1.27
Cu-β-Zeolite	1.4	4.30	4.29

3.3. Performance of hybrid catalysts (Cu-Zn/Cu-β) as a function of copper content

A group of modified β-zeolite was prepared with different Cu contents by an incipient wetness impregnation method; Fig. 6 and 7 shows their performance combined with a Cu-Zn methanol synthesis catalyst in a light hydrocarbon synthesis reaction.

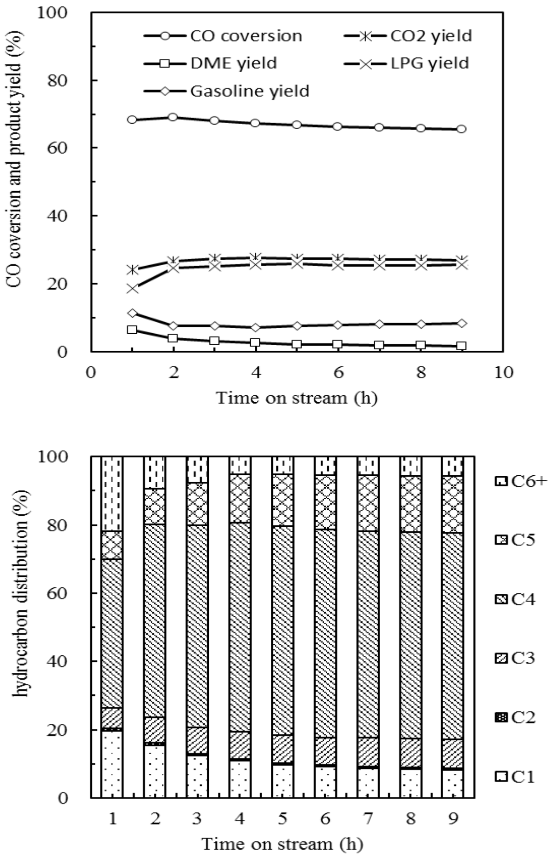


Fig. 6 Performance of hybrid catalysts (Cu-Zn/1.4%(wt)Cu-β) in a slurry phase

3.5 MPa, 280 ℃, H_2/CO=2, flow of syngas=80ml/min, (Cu-Zn)/1.4%(wt)Cu-β= 1/4 (by weight)

Compared Fig. 6 to Fig. 5, the absence of Pd in a zeolite decreases the methane selectivity in products which is favourable because methane is the most unwanted product in this process. Our experimental results have demonstrated that Pd has high hydrogenation activity of CO into methane or the pyrolysis of DME to water and methane.

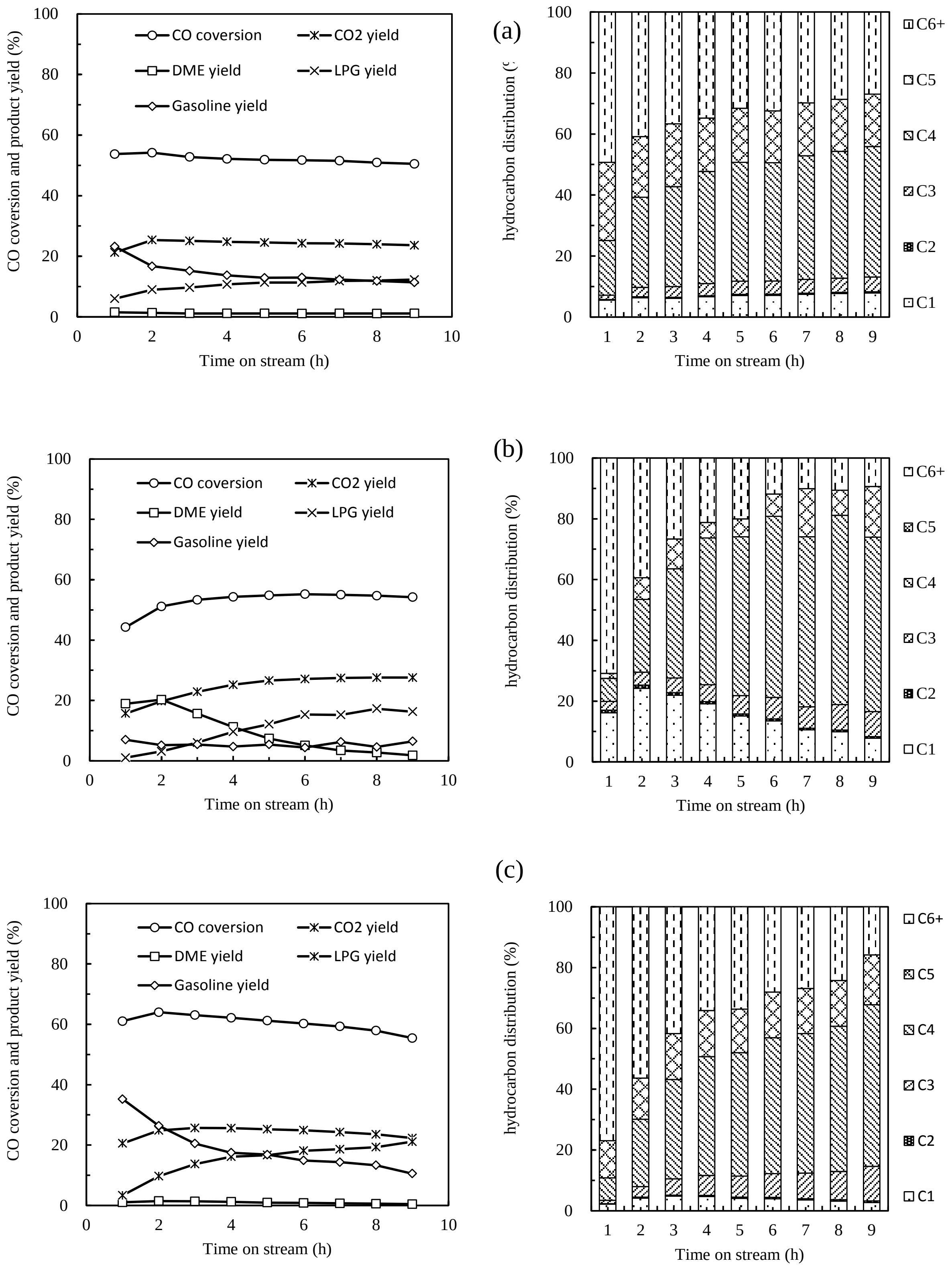


Fig. 7 Performance of hybrid catalysts (Cu-Zn/Cu-β) in a slurry phase

3.5 MPa, 280 ℃, $H_2/CO=2$, flow of syngas=80ml/min,

(a) (Cu-Zn)/0.5%(wt)Cu-β= 1/4 (by weight)

(b) (Cu-Zn)/2.9%(wt)Cu-β= 1/4 (by weight)

(c) (Cu-Zn)/5.0%(wt)Cu-β= 1/4 (by weight)

The addition of copper into a zeolite has two functions: the elimination of water formation and the hydrogenation of olefins. When the Cu content is low in the zeolite, the hybrid catalyst has insufficient activity for the water-gas shift reaction. The DME yield and CO conversion is low when the catalyst contains 0.5%(wt) Cu while a catalyst containing more than 2.9%(wt) Cu produces significantly heavier hydrocarbons and low conversion of CO. Also, in a catalyst containing 5.0 %(wt) Cu, the catalyst had low stability with time on stream. Fig. 8 shows the TPD of NH_3 over reduced modified zeolites. TPD results demonstrated that Cu introduction decreased the acid strength and high content of Cu as well as a decrease in the quantity and acidic strength of zeolite which resulted in low activity of methanol conversion. The low acidic strength of zeolite generated a low pyrolysis ability of long chain hydrocarbons from a short chain hydrocarbon which resulted in heavier hydrocarbons in the product. Considering the activity, stability and selectivity for LPG, a β-zeolite containing 1.4%(wt)Cu is the best catalyst for LPG synthesis in the slurry phase.

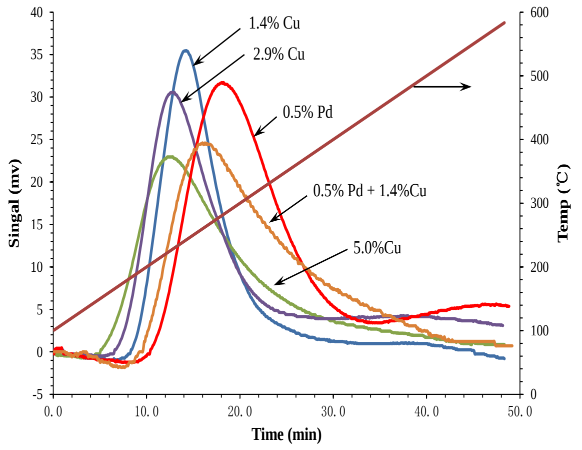


Fig. 8 TPD of NH_3 over reduced modified zeolites

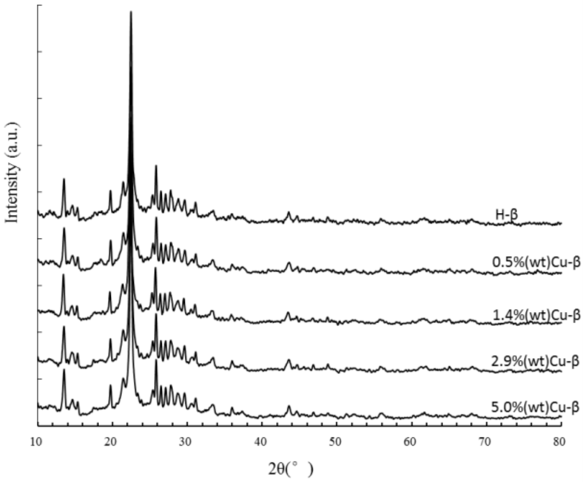


Fig. 9 XRD spectra of catalysts

By comparing the performance of the hybrid catalyst containing modified a β-zeolite, 1.4%(wt)Cu replacement of Pd not only increased the reactivity and stability of the hybrid catalyst, but also increased the selectivity of LPG in the product. Furthermore, Cu replacement of Pd decreases the commercial application cost of the direct synthesis of light hydrocarbons from syngas.

The samples of modified β-zeolite were examined by X-ray diffraction to determine the chemical form and crystallite size. As Fig. 9 shows, the catalyst composed of supported Cu on β-zeolite (calcined) showed almost no difference compared to XRD spectra of β-zeolite. No typical peak of CuO demonstrated that copper oxide was well dispersed in β-zeolite after precipitation and calcination. The crystallite size of CuO is no more than 4 nm.

3.4. Stability of hybrid catalysts in the slurry phase

As Fig. 10 shows, the hybrid catalyst Cu-Zn/1.4%(wt)Cu-β demonstrated a high activity of reaction and low selectivity for CO_2 at 280℃ and 3.5 MPa. Its activity decreased slowly with time on stream. The CO conversion decreased about 2% after 48hr. The hybrid catalyst showed a stable activity for synthesis of light hydrocarbon synthesis, while the selectivity of CO_2 was also the same low.

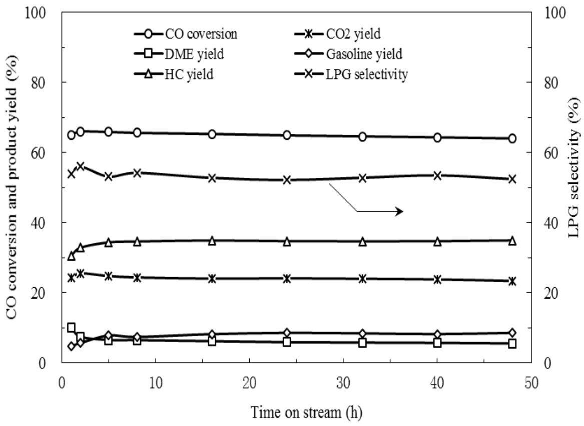


Fig. 10 Performance of hybrid catalysts (Cu-Zn/1.4%(wt)Cu-β) in a slurry phase as a function of time on stream
3.5 MPa, 280 ℃, $H_2/CO=2$, flow of syngas=80ml/min, (Cu-Zn)/1.4%(wt)Cu-β= 1/4 (by weight)

The reaction of syngas hydrogenation in gas phase over catalyst is inevitably accompanied by local overheating of catalyst surface. Local overheating of catalyst may lead to the deactivation of catalyst and also to the increase in methane selectivity. Slurry phase reaction system helped emission of water from the surface of catalyst and depressed the water shift reaction. Moreover, the production of undesirable products can be reduced under the fluid phase reaction system and the deactivation of the catalyst can be mitigated through better heat and mass transfer, consequently prolonging the longevity of catalyst

Owing to the advantages mentioned above the hybrid catalyst Cu-Zn/1.4%(wt)Cu-β in the slurry phase is promising for commercial application of direct synthesis of light hydrocarbon synthesis from syngas.

4. Conclusions

The synthesis of light hydrocarbon over the hybrid catalyst Cu-Zn/Cu-β(300) in the slurry phase demonstrated high activity and reaction stability. The reaction in slurry phase systems with an inert fluid n-cetane has been developed to overcome the problems of catalyst surface local overheating in the gas-phase process. The presence of water in a zeolite impairs ability of zeolite to convert methanol to hydrocarbons. Cu replacement of Pd supported on a β-zeolite increased the activity and stability of the catalyst and the selectivity of LPG by the removal of water from the zeolite. The slurry reaction system has promising applications in the direct synthesis of light hydrocarbon from syngas.

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