生物质炭和富二氧化碳合成气制取二甲醚

徐 勇 颜世志 叶同奇 张 钊 李全新*

(中国科学技术大学化学物理系, 生物质洁净能源实验室, 合肥 230026)

摘要: 研究了一种利用富二氧化碳合成气和生物质炭联合制取二甲醚的方法, 其过程包括两个步骤: 富二氧化碳合成气调整以及调整后合成气合成二甲醚。在合成气调整过程中, 利用生物质炭为原料在 $\text{Ni}/\text{Al}_2\text{O}_3$ 催化剂上将富二氧化碳合成气调整为富一氧化碳合成气。经过 $800\text{ }^\circ\text{C}$ 合成气调整后, 合成气中 CO_2 含量大幅降低而 CO 含量大幅提高, CO_2/CO 的摩尔比从原始合成气的 6.33 降至 0.21。然后, 分别用调整前后的合成气合成二甲醚, 结果表明, 经过调整后, C 转化率得到很大的提高, 二甲醚产率比调整前高 4 倍。本工作提供了一种可利用富二氧化碳生物质合成气制取燃料的途径, 并且提供了一种新的利用生物质炭的方法。

关键词: 生物质炭; 二甲醚; 生物质合成气调整; $\text{Ni}/\text{Al}_2\text{O}_3$ 催化剂; $\text{Cu-ZnO-Al}_2\text{O}_3/\text{HZSM-5}$ 催化剂

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Dimethyl Ether Production from Biomass Char and CO_2 -Rich Bio-Syngas

XU Yong YAN Shi-Zhi YE Tong-Qi ZHANG Zhao LI Quan-Xin*

(Department of Chemical Physics, Anhui Key Laboratory of Biomass Clean Energy, University of Science and Technology of China, Hefei 230026, P. R. China)

Abstract: We report on a novel approach toward dimethyl ether (DME) synthesis using crude CO_2 -rich bio-syngas and biomass char. The crude bio-syngas was derived from bio-oil reforming and was initially conditioned by catalytic conversion into CO -rich bio-syngas using biomass char over the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst. The molar ratio of CO_2 to CO significantly decreased from 6.33 in the CO_2 -rich bio-syngas to 0.21 after bio-syngas conditioning at $800\text{ }^\circ\text{C}$. The yield of dimethyl ether from the conditioned bio-syngas was about four times higher than that from the CO_2 -rich bio-syngas over the $\text{Cu-ZnO-Al}_2\text{O}_3/\text{HZSM-5}$ catalyst. This work potentially provides a useful approach toward producing biofuels and chemicals from bio-syngas and a novel utilization of biomass char.

Key Words: Biomass char; Dimethyl ether; Bio-syngas conditioning; $\text{NiO-Al}_2\text{O}_3$ catalyst; $\text{Cu-ZnO-Al}_2\text{O}_3/\text{HZSM-5}$ catalyst

1 Introduction

Increasing concerns about the increasing energy demand, global climate changes, depletion of fossil fuel resources, and rise of oil price have pushed the renewable energy such as biomass energy to the hotspot topics in recent years.^{1,2} Biomass is

a rich, environmentally friendly and renewable resource which is globally available, and can be used as an alternative feedstock for energy source or chemicals.^{3,4} As an only renewable carbon resource, biomass can be converted from solid phase into a wide range of liquid fuels (called as bio-fuels) or chemi-

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*Corresponding author. Email: liqx@ustc.edu.cn; Tel: +86-551-3601118.

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cals based on the thermochemical and biochemical processes, including bio-oil, bio-methanol, bio-ethanol, bio-diesel, liquid hydrocarbons (e.g., gasoline, diesel, waxes), mixed alcohols, DME, acetic acid, and formaldehyde.^{5,6}

To produce biofuels or chemicals from bio-syngas, the main procedures generally include the production of bio-syngas, syngas conditioning, and fuel synthesis. Bio-syngas can be produced from biomass gasification and bio-oil reforming.^{7,8} However, these bio-syngases, generally, are rich in CO₂.⁹ In principle, the CO₂-rich bio-syngas is possible for bio-fuels through CO₂ hydrogenation, but the fuel yield is much lower than that from CO-rich syngas. To obtain a higher fuel yield, the CO₂-rich bio-syngas should be adjusted to meet the conventional fuel synthesis processes by decreasing CO₂ content and increasing CO content.

DME is a useful chemical intermediate for the production of many important chemicals such as dimethyl sulfate, methyl acetate, and light olefins.¹⁰ As the oil resources are expected to deplete in near future, alternative fuels, such as biomass-derived DME and methanol, have been getting greater attention to minimize the emissions of global warming gases and hazardous components such as SO_x, NO_x, and particulate matter, and the application of DME as an alternative diesel fuel has been proposed recently.¹¹ In our previous work, attention has been paid to producing hydrogen, bio-syngas, and bio-fuels such as methanol and Fischer-Tropsch synthesis fuels from bio-oil.^{8,12–15} Present work aims to convert the CO₂-rich bio-syngas into CO-rich bio-syngas using biomass char and to efficiently produce DME from the bio-syngas.

2 Experimental

2.1 Catalyst preparation and characterization

Biomass chars were produced by fast pyrolysis of biomass in a fixed-bed reactor at a final pyrolysis temperature of 500 °C. Some properties are listed in Table 1. The activated carbon (analytical reagent) was purchased from Sinopharm Chemical Reagent Co., Ltd. in China. HZSM-5 (with a SiO₂/Al₂O₃ molar ratio of 25) was provided by Nankai University. The Cu-ZnO-Al₂O₃ catalyst was purchased from Jingjiang Company in China.

Table 1 Main characteristic of the used husk char and the sawdust char

Feedstock	Main characteristics	
	ultimate analysis	proximate analysis
Husk char	C: 45.38%	Fixed carbon: 35.7%
	H: 1.34%	Ash: 35.0%
	N: 0.93%	Volatile matter: 10.9%
	O: 52.35%	Moisture: 5.6%
Sawdust char	C: 65.16%	Fixed carbon: 54.5%
	H: 2.94%	Ash: 15.3%
	N: 0.33%	Volatile matter: 18.1%
	O: 31.57%	Moisture: 4.8%

^aby difference

The NiO-Al₂O₃ catalyst for the bio-syngas conditioning was prepared by the coprecipitation of the metallic nitrate mixture (Ni and Al) with K₂CO₃. The prepared process details were described elsewhere.¹⁶ Cu-ZnO-Al₂O₃/HZSM-5 was prepared by physically mixing the powders (under 150 meshes) of HZSM-5 and Cu-ZnO-Al₂O₃ catalyst with a mass ratio of 1:2.¹⁷ The contents of metallic oxide in the resulting samples were measured by inductively coupled plasma and atomic emission spectroscopy (ICP/AES, Atom scan Advantage of Thermo Jarrell Ash Corporation, USA). The Brunauer-Emmett-Teller (BET) surface area, pore volume, and average pore size were evaluated from the N₂ adsorption-desorption isotherms obtained at 77 K using a COULTER SA 3100 analyzer. X-ray diffraction (XRD) was performed to determine the bulk crystalline phases of catalyst. It was measured on an X'pert Pro Philips diffractometer with a Cu K_α radiation (λ=0.15418 nm).

2.2 Reaction systems

The conditioning of CO₂-rich bio-syngas was evaluated in a fixed-bed continuous-flowing quartz tube reactor at atmospheric pressure. The mixture of NiO-Al₂O₃ catalyst and biomass char with a certain mass ratio was installed in the center of the reactor. Before reaction, the catalysts were reduced by hydrogen at 500 °C for 2 h. The gases were fed into the reactor and controlled by a mass flow controller, and the effluent gases from the reactors were measured by flow display. Temperature was measured by the thermocouples inserted into the catalyst bed. DME synthesis was carried out in a fixed-bed continuous-flowing stainless steel reactor. Generally, 1.0 g catalyst diluted with a 2.0 mL Pyrex beads, was used for each test. Before reaction, the catalysts were reduced by hydrogen (10% (φ) in Ar) at 260 °C for 6 h. Then, bio-syngas was conducted to the reactor for DME synthesis under a setup synthesis condition. H₂, N₂, CO, and CO₂ were detected by a gas chromatograph (Model: SP6890, column: TDX-01) with a thermal conductivity detector. DME, CH₃OH, and hydrocarbons were detected by another gas chromatograph (Model: SP6890, column: PorapakQ-S, USA) with a flame ionization detector. Ultra-high-purity argon (99.999%) was used as the carrier gas. The performance of the bio-syngas conditioning and DME synthesis was evaluated by the following Eqs. (1–5):

$$C_{\text{CO}_2} = \frac{n_{\text{CO}_2, \text{in}} - n_{\text{CO}_2, \text{out}}}{n_{\text{CO}_2, \text{in}}} \times 100\% \quad (1)$$

$$Y_{\text{CO}} = \frac{n_{\text{CO}, \text{out}} - n_{\text{CO}, \text{in}}}{n_{\text{CO}_2, \text{in}}} \times 100\% \quad (2)$$

$$C_{\text{CO}} = \frac{n_{\text{CO}, \text{in}} - n_{\text{CO}, \text{out}}}{n_{\text{CO}, \text{in}}} \times 100\% \quad (3)$$

$$Y_{\text{DME}} = \frac{2n_{\text{DME}, \text{out}}}{n_{\text{C}, \text{in}}} \times 100\% \quad (4)$$

$$S_X = \frac{mn_X}{n_{\text{C}, \text{in}} - n_{\text{C}, \text{out}}} \quad (5)$$

where X represents DME, CH₃OH, hydrocarbons, CO, CO₂; *m* represents the carbon numbers of X; *C*, *Y*, and *S* represent conversion, yield, and selectivity, respectively.

3 Results and discussion

3.1 Catalyst characterizations

The nickel loading in the resulting NiO-Al₂O₃ sample was about 18.6% (w) NiO, and CuO and ZnO loading in Cu-ZnO-Al₂O₃ sample were 63.1% and 27.3% respectively from ICP-AES results. The BET surface area, pore volume, and average pore size of the catalysts are listed in Table 2.

XRD patterns of different catalysts are shown in Fig.1. The diffraction peaks of NiO, Al₂O₃, and NiAl₂O₄ were observed from the fresh catalyst. Three characteristic peaks at 2 θ of 44.4°, 51.9°, and 76.4° were identified from the used catalyst, corresponding to the diffractions of Ni. This indicates that NiO is reduced to the metallic Ni by H₂. XRD patterns of the Cu-ZnO-Al₂O₃ catalyst are shown in Fig.1b. Phase due to CuO and its reflections at 2 θ of 35.5°, 38.6°, and 48.8° were observed in the fresh Cu-ZnO-Al₂O₃ catalyst, the characteristic peaks of ZnO and Al₂O₃ were also identified. After reduction, the characteristic peaks of Cu were identified at 2 θ of 50.6° and 74.1°. In ad-

dition, the typical XRD patterns from the fresh HZSM-5 and the reduced HZSM-5 suggested that the HZSM-5 structure was retained after reaction.

3.2 Effect of the mass ratio of catalyst to carbon ($R_{C/C}$) on the CO₂-rich bio-syngas conditioning

To further understand the effects of $R_{C/C}$ on the conditioning of CO₂-rich bio-syngas over Ni/Al₂O₃, the present conditioning was carried out at various $R_{C/C}$ values from 0 to 2.0, the reaction temperature and flow rate were kept constant at 700 °C and 1200 L·kg⁻¹·h⁻¹, respectively. As shown in Fig.2, a further increase in $R_{C/C}$ from 0 to 1.0 resulted in a significant increase in the CO₂ conversion and CO yield, but tended towards saturation when $R_{C/C}$ was over 1.0. The CO₂ conversion increased from about 25.4% to 58.4% when $R_{C/C}$ increased from 0 to 1.0. In particular, a slight increase in CO₂ conversion and CO yield was observed when $R_{C/C}$ increased from 1.0 to 2.0. The above results suggest that the performance of Ni/Al₂O₃ catalyst for the CO₂-rich bio-syngas conditioning can remarkably enhanced. The observed effects of Ni/Al₂O₃ catalyst should be attributed to the dissociation of CO₂ on the surface of Ni. Ni/Al₂O₃ catalyst was widely used for the reforming of CH₄ with CO₂ to syngas.¹⁸⁻²⁰ Previous work^{21,22} has proved the dissociation of CO₂ on surface of Ni (CO₂(a) → CO(a) + O(a)).

3.3 Effect of temperature on the CO₂-rich bio-syngas conditioning

To investigate the effect of temperature on catalytic perfor-

Fig.1 (a) XRD patterns of the fresh (A) and reduced (B) NiO-Al₂O₃; (b) XRD patterns of the fresh (A) and reduced (B) Cu-ZnO-Al₂O₃ catalyst; (c) XRD patterns of the fresh (A) and reduced (B) HZSM-5

Fig.2 Effect of $R_{C/C}$ on CO₂ conversion (a) and CO yield (b) in the CO₂-rich bio-syngas conditioning

$T=700$ °C, flow rate=1200 L·kg⁻¹·h⁻¹

mance, the conditioning of CO₂-rich syngas was carried out over Ni/Al₂O₃ at various temperature (400–800 °C), with a flow rate of 1200 L·kg⁻¹·h⁻¹ and R_{CC} of 1. Fig.3 presents the effects of temperature on the performance of the bio-syngas conditioning. It was observed that, by increasing the reaction temperature from 500 to 800 °C at a constant R_{CC} of 1.0, there was a sharp increase in the CO₂ conversion and CO yield. The CO₂ conversion remarkably increased from 36.2% at 500 °C to 71.6% at 800 °C, and CO yield increased from 23% to 90%. The main composition of the crude bio-syngas changed from $V(H_2)/V(CO)/V(CO_2)=68.6/4.1/26.0$ in the crude bio-syngas to $V(H_2)/V(CO)/V(CO_2)=59.3/30.9/6.8$ after the conditioning at 800 °C. In particular, the concentration of CH₄ decreases with increasing the temperature, and can not be detected over 700 °C. The above results showed that the CO₂ conversion and CO yield were significantly enhanced by increasing temperature. The reasons are summarized as follows: firstly, both the Boudouard reaction ($CO_2+C=2CO$) and reverse water gas shift (RWGS) reaction ($CO_2+H_2=CO+H_2O$) involved in the bio-syngas conditioning are endothermic in thermodynamics. A recent work on the kinetics of char gasification with CO₂ claims that the increasing temperature shows a positive influence on the apparent activation energy, accompanied with an increase of gasification rate.²³ Accordingly, a higher temperature will accelerate the rates of Boudouard reaction and RWGS reaction, leading to an increase of converting CO₂ into CO in the bio-syngas conditioning. Secondly, high temperature may promote the dis-

sociation of CO₂ on Ni, leading a further conversion of CO₂ to CO.

3.4 Effect of flow rate on the CO₂-rich bio-syngas conditioning

To further understand the effect of flow rate on catalytic performance of NiO-Al₂O₃ catalyst, the conditioning of CO₂-rich bio-syngas was carried out at various flow rate (300–1500 L·kg⁻¹·h⁻¹), at 700 °C and R_{CC} of 1.0. As shown in Fig.4, at a flow rate of 300 L·kg⁻¹·h⁻¹, CO₂ conversion and CO yield were about 76.7% and 107%. With increasing the flow rate to 1500 L·kg⁻¹·h⁻¹, CO₂ conversion and CO yield decreased to 61% and 61%, respectively. The results suggest that an increase in flow rate leads to a decrease in CO₂ conversion and CO yield in the bio-syngas conditioning, which can be attributed to the residence time of biomass char and the CO₂-rich bio-syngas in the catalyst bed is shortened by increasing flow rate.

3.5 DME synthesis

For a comparison, the crude CO₂-rich bio-syngas ($V(H_2)/V(CO)/V(CO_2)=68.6/4.1/26$) and the conditioned bio-syngas ($V(H_2)/V(CO)/V(CO_2)=59.3/30.9/6.8$) were tested for DME synthesis. The gas composition of the conditioned syngas was close to coal derived syngas, previous works have reported DME synthesis from coal syngas.^{24,25} For DME synthesis from the crude CO₂-rich bio-syngas, as shown in Table 3, CO₂ conversion increased from 5% to 15.1% with the increasing temperature from 240 to 320 °C. An increase in the DME selectivi-

Fig.3 Effect of temperature on CO₂ conversion (a), CO yield (b), gas composition (c), and n_{CO_2}/n_{CO} (d) in the CO₂-rich bio-syngas conditioning

$T=500-800$ °C, flow rate=1200 L·kg⁻¹·h⁻¹, $R_{CC}=1.0$

Fig.4 Effect of flow rate on CO_2 conversion (a), CO yield (b), gas composition (c), and $n(\text{CO}_2)/n(\text{CO})$ (d) in the CO_2 -rich bio-syngas conditioning

$T=700\text{ }^\circ\text{C}$, $R_{\text{GC}}=1.0$

ty was observed when temperature increased from 240 to 280 $^\circ\text{C}$, but decreased with a further increasing temperature over 280 $^\circ\text{C}$. Table 4 presents the performance of the DME synthesis from the conditioned bio-syngas, CO conversion increased from 72.5% to 84.8% as temperature increased from 240 to 280 $^\circ\text{C}$, but a decreasing CO conversion was observed when temperature was higher than 280 $^\circ\text{C}$. The maximum conversion and DME yield were 84.8% and 65.5% respectively at 280 $^\circ\text{C}$. The above results indicated that the performance of the DME synthesis was significantly enhanced *via* the bio-syngas conditioning.

A generic accepted mechanism of DME synthesis from syngas over Cu-ZnO- Al_2O_3 /HZSM-5 includes two sequential steps: methanol synthesis from syngas and the dehydration of methanol to DME, and the methanol synthesis reaction is the rate-limiting step in the direct DME synthesis from syngas.²⁶ Consequently, the different results of DME synthesis should be attributed to the different mechanism of methanol formation through CO hydrogenation and CO_2 hydrogenation. For CO hydrogenation, the mechanism of methanol formation over the Cu-based catalyst is “the formyl intermediate formation mechanism”, and the Cu crystallites in the catalyst have been identi-

Table 3 Effect of temperature on DME synthesis from the crude CO_2 -rich bio-syngas over the Cu-ZnO- Al_2O_3 /HZSM-5 catalyst

$T/^\circ\text{C}$	GHSV/ h^{-1}	p/MPa	$C_{\text{CO}_2}/\%$	$Y_{\text{DME}}/\%$	$S_{\text{DME}}/\%$	$S_{\text{CH}_3\text{OH}}/\%$	$S_{\text{CO}}/\%$	$S_{\text{CH}_4}/\%$
240	2000	4	5.0	55.1	44.4	—	0.5	5.55
260	2000	4	12.1	75.7	23.5	—	0.8	11.8
280	2000	4	13.3	84.5	13.9	—	1.6	12.7
300	2000	4	14.2	80.5	4.3	10.6	4.6	11.2
320	2000	4	15.1	45.9	0.8	46.2	7.1	6.91

GHSV: gas hourly space velocity

Table 4 Effect of temperature on DME synthesis from the conditioned bio-syngas over the Cu-ZnO- Al_2O_3 /HZSM-5 catalyst

$T/^\circ\text{C}$	GHSV/ h^{-1}	p/MPa	$C_{\text{CO}_2}/\%$	$Y_{\text{DME}}/\%$	$S_{\text{DME}}/\%$	$S_{\text{CH}_3\text{OH}}/\%$	$S_{\text{CO}}/\%$	$S_{\text{CH}_4}/\%$
240	2000	4	72.5	40.0	36.5	23.4	0.1	31.9
260	2000	4	81.3	52.7	20.2	26.9	0.2	42.8
280	2000	4	84.8	65.5	4.0	30.1	0.4	60.1
300	2000	4	84.3	58.2	3.5	35.5	2.8	49.0
320	2000	4	71.6	52.7	1.1	37.6	8.6	40.9

Fig.5 (a) Catalysts stability during the bio-syngas conditioning, (b) catalysts stability during the DME synthesis from the conditioned syngas

fied as the active catalytic sites.²⁷ Alternatively, the formation and hydrogenation of the formate intermediate are thought to be the key steps to produce methanol from CO₂ hydrogenation.^{28–30} Another reason is water produced *via* the RWGS reaction in CO₂ hydrogenation may block the active sites on the catalyst surface.

3.6 Stability of catalysts

The stability of the Ni/Al₂O₃ catalyst in bio-syngas conditioning process was tested by measuring the CO₂ conversion and CO yield as a function of the time on stream. As shown in Fig.5a, no obvious changes are observed for about 50 h under the reaction conditions ($T=800\text{ }^{\circ}\text{C}$, $R_{\text{C/C}}=1.0$, flow rate $=1200\text{ L}\cdot\text{kg}^{-1}\cdot\text{h}^{-1}$) in the conditioning process. It clearly shows that both the CO₂ conversion and CO yield remained essentially constant for the whole test period, which indicates that no noticeable deactivation of the catalyst is occurring. On the other hand, no noticeable deactivation of the Cu-ZnO-Al₂O₃/HZSM-5 catalyst was observed in DME synthesis process (Fig.5b).

4 Conclusions

This work reported a novel approach of DME synthesis from the CO₂-rich bio-syngas, including two steps: the CO₂-rich bio-syngas conditioning using biomass char and DME synthesis from the conditioned bio-syngas. For the bio-syngas conditioning, the CO₂ conversion and CO yield reached a level as high as 71.1% and 89% at 800 °C, respectively, CO₂/CO molar ratio significantly dropped from 6.33 to 0.21. For the DME synthesis, the maximal CO conversion and DME yield were 84.8% and 65.5%, which were much higher than those from the CO₂-rich bio-syngas. Present work may provide a useful method for DME synthesis from the CO₂-rich bio-syngas, and a novel utilization of biomass char.

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