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Production of Light Olefins from Biosyngas by Two-stage Catalytic Conversion Process via Dimethyl Ether

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(Dated: Received on October 16, 2013; Accepted on December 10, 2013)

NiSAPO-34 and NiSAPO-34/HZSM-5 were prepared and evaluated for the performance of dimethyl ether (DME) conversion to light olefins (DTO). The processes of two-stage light olefin production, DME synthesis and the following DTO, were also investigated using biosyngas as feed gas over Cu/Zn/Al/HZSM-5 and the optimized 2%NiSAPO-34/HZSM-5. The results indicated that adding 2%Ni to SAPO-34 did not change its topology structure, but resulted in the forming of the moderately strong acidity with decreasing acid amounts, which slightly enhanced DME conversion activity and C₂=-C₃= selectivity. Mechanically mixing 2%NiSAPO-34 with HZSM-5 at the weight ratio of 3.0 further prolonged DME conversion activity to be more than 3 h, which was due to the stable acid sites from HZSM-5. The highest selectivity to light olefins of 90.8% was achieved at 2 h time on stream. The application of the optimized 2%NiSAPO-34/HZSM-5 in the second-stage reactor for DTO reaction showed that the catalytic activity was steady for more than 5 h and light olefin yield was as high as 84.6 g/m³_{syngas} when the biosyngas (H₂/CO/CO₂/N₂/CH₄=41.5/26.9/14.2/14.6/2.89, vol%) with low H/C ratio of 1.0 was used as feed gas.

Key words: Light olefins, Two-stage conversion, Dimethyl ether, Biosyngas, NiSAPO-34/HZSM-5

I. INTRODUCTION

The increasing demand for light olefins (C₂=-C₄=) has led to the development on new synthesis processes, using natural gas, coal, and biomass [1]. Several technical processes have been applied, such as methane oxidative coupling, Benson process, and direct (or indirect) syngas conversion [2]. Indirect syngas conversion to low carbon olefins usually include two reactions: syngas conversion to intermediates like methanol and dimethyl ether (DME), followed by methanol (or DME) to olefin process (MTO or DTO) over SAPO-34- and ZSM-5-based catalysts. The conversion of syngas to DME was reported to have a synergistic effect to break thermodynamic equilibrium barrier in the separated reactions of methanol synthesis and methanol dehydration over hybrid catalyst of Cu/Zn/Al/zeolite catalyst [3, 4]. Also high selectivity to light olefins and thermal stability provide DTO considerable advantages over MTO process [5, 6]. Thus two-stage process for light olefin production, direct DME synthesis and the following DTO,

seems promising due to the efficiency and flexibility of each stage [7, 8].

ZSM-5, medium-pore zeolite composed of intersecting straight (0.53 nm×0.56 nm) and sinusoidal (0.51 nm×0.55 nm) 10-ring channels, has been studied for propylene production with excellent durability. Yet its strong acidity and large pore size of 0.55 nm would result in further oligomerization with high yield to aromatics [9, 10]. While moderate acidic SAPO-34, consisting of ellipsoidal 20-hedral cages of 0.67 nm×1.0 nm interconnected via 8-ring windows with pore openings of 0.38 nm×0.38 nm, is proper for high yield to ethylene [11]. However its quick deactivation was obvious due to the coke deposition and pore blocking in the small pores. Numerous efforts are made to prolong its lifetime, including the addition of basic metal oxides or transition metals, decreasing silicon content, and so on [12, 13]. Among them, NiSAPO-34 exhibited great advantages toward ethylene yield [14].

Although plenty of modification methods for SAPO-34 and ZSM-5 catalysts have been tested for DTO processes, few studies have focused on the mixture of these two zeolites [15]. In the present work, nickel modified SAPO-34 and mechanical mixture of NiSAPO-34/HZSM-5 were prepared and tested for DTO perfor-

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mance. And the optimized DTO catalyst was applied to the second-stage reactor for indirect light olefin production via DME, following the fixed-bed DME synthesis reactor using biosyngas as feed gas. The composition, acidity and phase morphology of the catalysts, as well as the composition of biosyngas, were investigated to evaluate the performance of light olefin synthesis.

II. EXPERIMENTS

A. Catalysts and characterization

DME synthesis catalyst, Cu/Zn/Al/HZSM-5, was prepared by co-precipitation method with acidic dehydration zeolite, the detail was reported in Ref.[16]. 2%NiSAPO-34 catalyst for DTO reaction was prepared by impregnation of nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Guangzhou Chemical Co., China) solutions over SAPO-34 zeolite (BET surface area of $573 \text{ m}^2/\text{g}$, pore volume of $0.36 \text{ m}^3/\text{g}$, Chemist Scientific Ltd., China). The nickel precursor was dissolved in water according to the designed weight amount, dried at $120 \text{ }^\circ\text{C}$ for 12 h, calcinated in air at $550 \text{ }^\circ\text{C}$ for 5 h. 2%NiSAPO-34/HZSM-5 was prepared by mechanical mixing of 2%NiSAPO-34 with HZSM-5 zeolite (BET surface area of $413 \text{ m}^2/\text{g}$, $\text{SiO}_2/\text{Al}_2\text{O}_3=19$, Nankai University catalyst Co. Ltd., China) at the weight ratio of 3.0. All samples were pressed under 15 MPa and sieved to 20–40 mesh. NH_3 -temperature programmed desorption (TPD) measurement was performed on a homemade TPD apparatus with TCD detector. Each sample (0.2 g) was first pre-treated at $600 \text{ }^\circ\text{C}$ for 3 h in He, cooled to $120 \text{ }^\circ\text{C}$, and then saturated with ammonia for 30 min. After purging with He for 1 h to remove the weakly absorbed ammonia, the analysis was carried out at a heating rate of $100 \text{ }^\circ\text{C}/\text{min}$ from $120 \text{ }^\circ\text{C}$ to $650 \text{ }^\circ\text{C}$. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku D/max-rC using Cu $K\alpha$ radiation.

B. Experimental setup and product

DTO reaction was operated at $400 \text{ }^\circ\text{C}$ and ambient pressure over 2.0 g SAPO-34-based catalyst in an quartz tube reactor (8 mm O.D.), fed by the gas flow with N_2/DME molar ratio of 8.25 at GHSV of 1500 h^{-1} . For the two-stage process of indirect light olefin synthesis, a stainless steel fixed-bed reactor and a quartz tube reactor were settled in sequence for DME synthesis and DTO reaction respectively. The first-stage of DME synthesis was carried out under condition of $P=5 \text{ MPa}$, $T=260 \text{ }^\circ\text{C}$ and $\text{GHSV}=3000 \text{ h}^{-1}$. In each run, 1.5 mL of Cu/Zn/Al/HZSM-5 was pre-reduced at $270 \text{ }^\circ\text{C}$ for 10 h with $5\% \text{ H}_2/95\% \text{ N}_2$. The effluent gas after DME synthesis was heated at $110 \text{ }^\circ\text{C}$, introduced to the second-stage reactor as feed gas. The tail gases from the reactor were kept warm at $110 \text{ }^\circ\text{C}$ and ana-

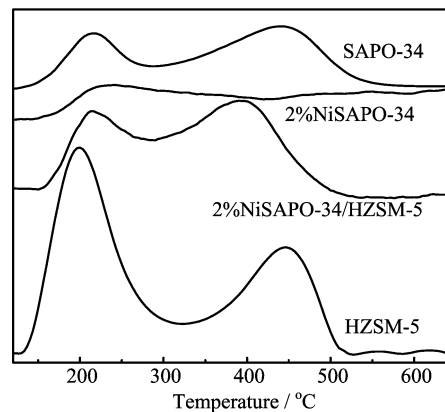


FIG. 1 NH_3 -TPD profiles of DTO catalysts.

lyzed online by two gas chromatographs. CO , N_2 , CH_4 , and CO_2 were analyzed by carbon-sieve column with TCD detector. Hydrocarbons and DME were analyzed by Porapak Q column with FID detector. The conversion of DME and CO and hydrocarbon selectivity were calculated on the balance of carbon.

III. RESULTS AND DISCUSSION

A. Acidity and structure properties of SAPO-34 based catalysts

SAPO-34 shows two NH_3 desorption peaks at 216 and $443 \text{ }^\circ\text{C}$ in Fig.1, corresponding to the weak and strong acid sites of 0.19 and $0.39 \text{ mmol}/\text{g}$ respectively. As a result, SAPO-34 presents a substantial amount of strong acidity [17, 18]. Compared to SAPO-34, 2%NiSAPO-34 exhibits higher desorption temperature of both weak and strong acid sites. And the desorption of NH_3 for the strong acidity continues above $650 \text{ }^\circ\text{C}$, which indicates that the moderately strong acid sites formed during Ni impregnated to SAPO-34. But the amount of total acid sites was sharply decreased, especially for the desorption maxima ascribed to strong acid sites. Only a small amount of weak acid sites of $0.15 \text{ mmol}/\text{g}$, corresponding to the desorption area at $120\text{--}350 \text{ }^\circ\text{C}$, were preserved. The decrease of acidity by Ni adding was probably due to the coverage of acid sites by Ni. Yet the topology structure for SAPO-34 crystals was kept over 2%NiSAPO-34, shown by the existence of the characteristic peaks of SAPO-34 crystals over 2%NiSAPO-34 in the XRD patterns of Fig.2. HZSM-5 showed a higher NH_3 desorption amount of $1.24 \text{ mmol}/\text{g}$ than SAPO-34.

The two unresolved desorption profiles at 213 and $390 \text{ }^\circ\text{C}$ were assigned to the weak and moderately strong acid sites over 2%NiSAPO-34/HZSM-5, when 2%NiSAPO-34 was mechanically mixed with HZSM-5 at the weight ratio of 3.0. HZSM-5 seems to have more effect on the acidity of 2%NiSAPO-34/HZSM-5 than 2%NiSAPO-34, which increased the moderately

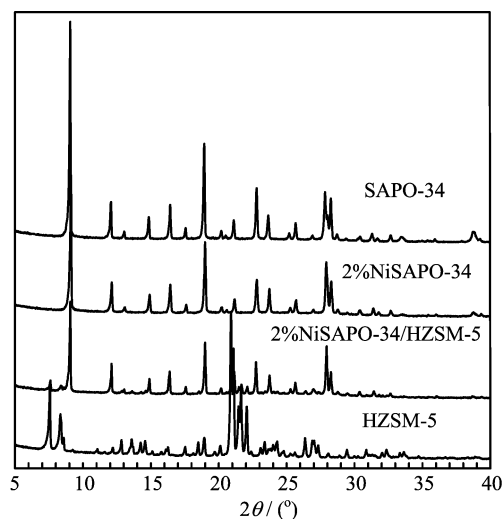


FIG. 2 XRD patterns of DTO catalysts.

strong acidity to 0.42 mmol/g. The decreased effect of 2%NiSAPO-34 on 2%NiSAPO-34/HZSM-5 is also supported by XRD results, which shows rapid intensity decrease for the characteristic peaks corresponding to SAPO-34 crystals. And the existence of the characteristic peaks for HZSM-5 at $2\theta=20^{\circ}$ – 30° and SAPO-34 at $2\theta=9.1^{\circ}$ and 18.9° indicated that the crystal structures of 2%Ni/SAPO-34 and HZSM-5 were not destroyed during mechanical mixing preparation, which affected DTO activity explained below.

B. Catalytic conversion of DME to light olefins

For the catalysts used, DME conversion decreased sharply when it was less than 80% as shown in Fig.3. DME conversion decreased to 41.2% and 12.3% after 45 min and 1.25 h time on stream (TOS) over SAPO-34 respectively. And the rapid catalyst deactivation was accompanied by high CH_4 selectivity of 10.9% at 1.25 h TOS in Fig.3(e). It might be due to the extra hydrogen drawing out from the residual hydrocarbon species on the high density of the strong acid sites in the small pores over SAPO-34 [19]. It was proportional to coke formation during hydride transfer and cyclization reactions during DTO reaction [20, 21]. The period with DME conversion higher than 80% was extended to 1 h over 2%NiSAPO-34, which probably resulted from its continuous distribution of acid sites at 230–650 °C in Fig.1. And the selectivity to $\text{C}_2^=$ and $\text{C}_3^=$ at 0.5 h TOS was 39.3% and 43.6% respectively, higher than that over SAPO-34. The smaller $\text{C}_2^=/\text{C}_3^=$ ratio of ca.0.9 also proved its longer DME conversion activity over 2%NiSAPO-34 than that over SAPO-34, since the increase of ethylene selectivity at the expense of $\text{C}_3^=$ selectivity is always a signal of pore volume decrease by coke deposition [19, 22, 23]. The prolonged DTO activity indicated that 2%Ni modification of SAPO-34 had

positive effect on light olefin production.

DME conversion was higher than 80% after 3 h TOS over 2%NiSAPO-34/HZSM-5. The highest light olefin yield of 90.8% was obtained at 2 h TOS in Fig.3(b). This could result from the small amount of HZSM-5 component in 2%NiSAPO-34/HZSM-5, which is unlikely to be deposited by coke due to its high content of weak acidity and relatively large pore diameter of 0.55 nm [24]. As DTO reaction continued, $\text{C}_2^=$ – $\text{C}_4^=$ yield and $\text{C}_3^=$ selectivity decreased simultaneously, which are the results of the suppressed formation of methyl benzenes to light olefins and coke deposition in the small pores of 2%NiSAPO-34 [25]. On the other hand, the product diffusion was hindered, thereby favored the smaller molecule as ethylene to diffuse over 2%NiSAPO-34/HZSM-5.

HZSM-5 was reported to show slow deactivation and some heavy hydrocarbons could be produced in DTO [26]. In this context C_5 – C_7 yield was less than 5%, determined by online GC fed by the heated tail gas. Since the amount of liquid hydrocarbons was usually small, it was in most cases measured without further analysis. The smallest $\text{C}_2^=/\text{C}_3^=$ ratio of 0.78–0.84 and $\text{C}_2^=$ selectivity of 25.4%–28.6% were obtained during 15 h TOS. While CH_4 selectivity increased to more than 8.26% after 2 h TOS, it could ascribe to the large amount of weak acid sites in Fig.1. $\text{C}_2^=/\text{C}_3^=$ ratio decreased over Ni and HZSM-5 added SAPO-34 catalyst, which was 1.85, 0.95, 0.85, and 0.80 respectively for SAPO-34, 2%NiSAPO-34, 2%NiSAPO-34/HZSM-5 and HZSM-5 at 1 h TOS. It further verified the increased DME conversion activity by Ni and HZSM-5 modification.

It was observed that the maximum $\text{C}_2^=$ selectivity was obtained at a longer TOS than that of $\text{C}_3^=$ over almost all catalysts in Fig.3, which was 38.0% at 45 min TOS and 29.7% at 30 min TOS over SAPO-34, 39.3% at 30 min TOS and 43.6% at 30 min TOS over 2%NiSAPO-34, 40.1% at 3 h TOS and 45.7% at 2 h TOS over 2%NiSAPO-34/HZSM-5, 28.6% at 5 h TOS and 32.7% at 3 h TOS over HZSM-5, respectively. It should result from the positive effect of coke deposition on $\text{C}_2^=$ formation, in terms of transition-state shape selectivity and acid distribution as explained by Chen [27]. The increased formation of coke with TOS suppressed the formation of larger intermediates, which were the precursors of higher olefins. Significant light olefin selectivity of 90.8% was observed at 2 h TOS with 100% DME conversion over 2%NiSAPO-34/HZSM-5, showing the combined advantage of SAPO-34 and HZSM-5. Although high DME conversion activity over 2%NiSAPO-34/HZSM-5 lasted only 3 h, shorter than HZSM-5, the former catalyst provided higher light olefin yield. That indicates great advantage of light olefin production if the catalyst regeneration is carried out simultaneously.

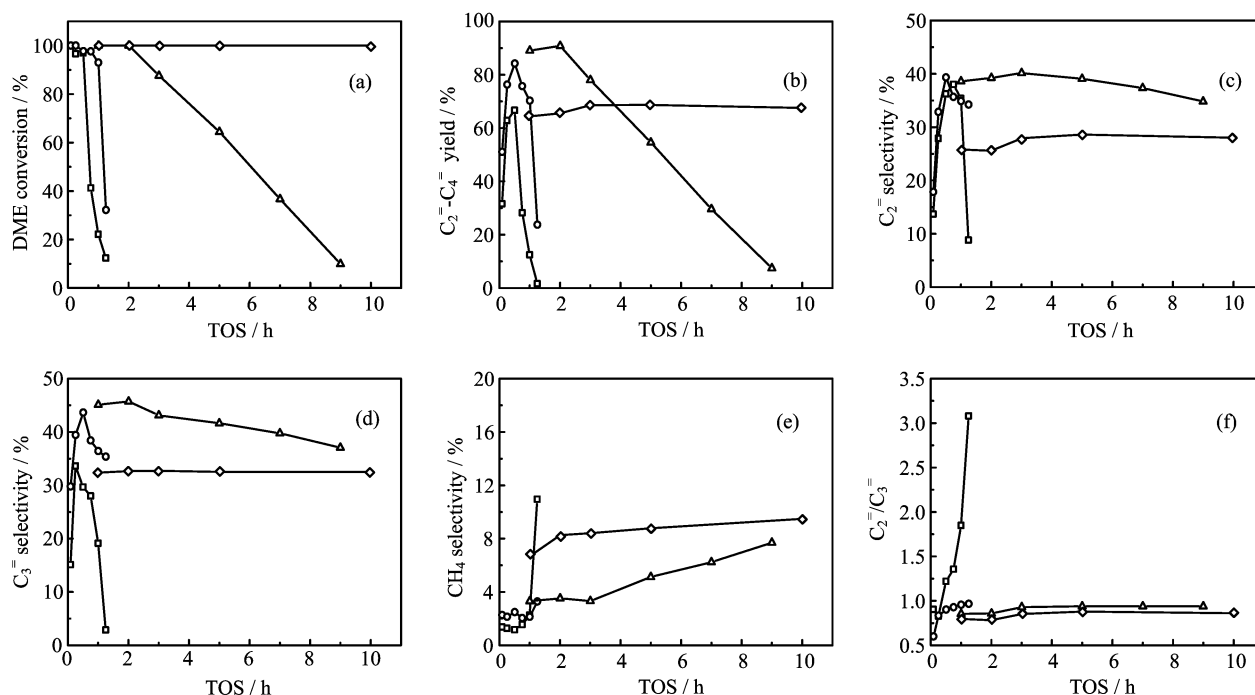


FIG. 3 Catalytic performance of DTO as a function of TOS over the catalysts including □ SAPO-34, ○ 2%Ni-SAPO-34, △ 2%Ni-SAPO-34/HZSM-5, ◇ HZSM-5.

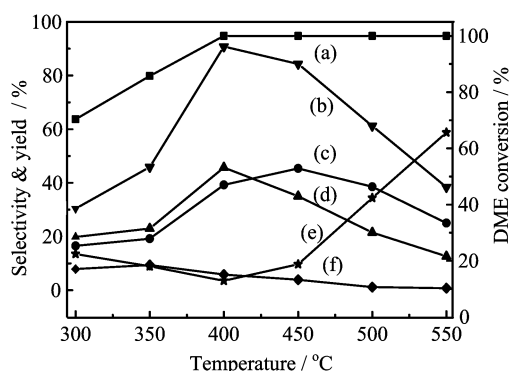


FIG. 4 Effect of reaction temperature on DTO performance over 2%Ni-SAPO-34/HZSM-5. (a) DME conversion, (b) C₂=-C₄ yield, (c) C₂H₄ selectivity, (d) C₃H₆ selectivity, (e) CH₄ selectivity, (f) C₄H₈ selectivity.

C. Effect of reaction temperature on DTO performance over 2%Ni-SAPO-34/HZSM-5

Figure 4 shows the effect of reaction temperature on DTO over the optimized 2%NiSAPO-34/HZSM-5 catalyst after 2 h TOS. DME conversion is incomplete (70.4%) with CH₄ selectivity of 13.5% at 300 °C. As the temperature increased to 550 °C, DME was completely converted. The highest C₄= selectivity of 9.4% was achieved at 350 °C, which gradually decreased with the increased temperature. The maximum C₃= selectivity of 45.7% was obtained at 400 °C, whereas C₂= selectivity steadily increased until 450 °C, which was

45.4%. After that, it decreased to 25% at 550 °C. C₂=/C₃= ratio increased from 0.83 at 300 °C to 0.86 at 400 °C and reached the maximum value of 1.98 at 550 °C. The increased C₂= selectivity with reaction temperature was related to the increased cracking of oligomers in the cages of NiSAPO-34. That might be the same reason that the maximum selectivity to C₃= and C₄= was obtained at lower temperature than that of C₂= selectivity.

The maximum yield for light olefins was 90.8% at 400 °C. Further increasing the reaction temperature caused the decomposition of DME to CH₄. The highest CH₄ selectivity was 58.8% at 550 °C due to thermal cracking of DME. High reaction temperatures also resulted in quick deactivation of 2%NiSAPO-34/HZSM-5 due to the accelerated coke formation. The weight loss of the used 2%NiSAPO-34/HZSM-5 under 2 h TOS and 400 °C is ca. 6.5%, corresponding to coke deposition amount of the catalyst.

D. Effect of diluting gas on DTO performance over 2%NiSAPO-34/HZSM-5

It was reported that the diluting gas could enhance MTO or DTO performance and prolong catalyst lifetime [28]. Because the effluent gas from DME synthesis contains H₂, CO, and CO₂ besides N₂, the effect of these diluting gases was investigated over 2%NiSAPO-34/HZSM-5 at 400 °C for DTO performance shown in Table I.

TABLE I Effect of diluting gas on DTO performance over 2%NiSAPO-34/HZSM-5. DME conversion is 100%.

Dilute gas	Product selectivity/%								
	C ₁	C ₂ ⁼	C ₂ ⁰	C ₃ ⁼	C ₃ ⁰	C ₄ ⁼	C ₄ ⁰	C ₂ ⁼ -C ₄ ⁼	C ₅ ⁺
N ₂	3.52	39.22	1.17	45.73	2.03	5.84	0.61	90.79	1.88
H ₂	5.17	32.49	5.46	30.95	9.41	7.66	2.65	71.1	6.21
CO	3.17	37.51	2.34	46.53	2.6	5.38	1.38	89.42	1.09
CO ₂	3.03	41.59	2.22	44.38	1.53	5.12	0.87	91.09	1.26

TABLE II The catalytic results of first-stage reaction conversion process of biosyngas to light olefins via DME.

Item	X _{CO} ^a /%	STY _{DME} /(g/mL h)	S _{DME+MeOH} /%	Effluent gas: H ₂ /CO/CO ₂ /N ₂ /CH ₄ /DME
Gas (A)	30.8	0.17	92	21.6/9.12/23.6/33.1/9.13/3.36
Gas (B)	46.8	0.46	95	14.6/29.1/9.54/24.7/9.57/12.0
Gas (C)	48.4	0.49	97	10.9/19.7/23.0/25.7/5.68/14.0

^a X_{CO} is CO conversion of biosyngas.

TABLE III The catalytic results of second-stage reaction conversion process of biosyngas to light olefins via DME. The conversion of DME and MeOH X_{DME+MeOH} is 100%.

Item	TOS ^a /h	Light alkene selectivity/%			Y ^b /(g/m ³ _{syngas})	Carbon utilization from syngas/%
		C ₂ ⁼	C ₃ ⁼	C ₄ ⁼		
Gas (A)	15	32.4	37.5	4.32	26.1	12.7
Gas (B)	7	36.8	40.6	4.74	77.1	31.4
Gas (C)	5	38.6	40.3	3.62	84.6	32.8

^a TOS is lifetime of 2%NiSAPO-34/HZSM-5.

^b Y is yield of C₂⁼+C₃⁼+C₄⁼.

Similar product selectivity was obtained under CO and N₂ diluting atmosphere. The slightly higher selectivity to C₂⁼ and light olefins under CO₂ condition may be ascribed to the reaction of C+CO₂→2CO, which consumes the coke formed in the pores of NiSAPO-34 and HZSM-5 as observed by Tan *et al.* [29]. Yet the low light olefin selectivity of 71.1% with increased selectivity to light alkanes of C₂⁰ and C₃⁰ under H₂ diluting condition could result from the hydrogenation of light olefins.

E. Two-stage process of biosyngas to light olefins via DME

The two-stage reaction process for light olefin production from biosyngas via DME was carried out, using Cu/Zn/Al/HZSM-5 and 2%NiSAPO-34/HZSM-5 for DME synthesis and DTO respectively. The effluent gas from the first-stage reactor for DME synthesis contained H₂, CO, CO₂, DME, N₂, methanol, and light hydrocarbons of C₁-C₃. It was introduced to the second-stage reactor without further separation. Three types of model biosyngas with low H₂/C ratio of ca.1.0 were used as feedstock, named as gas (A), gas (B) and gas (C). And the molar composition of H₂/CO/CO₂/N₂/CH₄ was

33.1/10.8/22.1/27.1/7.05, 40.0/33.8/5.54/15.2/5.57, and 41.5/26.9/14.2/ 14.6/2.89, respectively [30, 31].

The results of the two-stage reaction are listed in Table II and Table III. The selectivity to light olefin is 72.4%, 82.1%, and 82.5% respectively as gas (A), gas (B), and gas (C) were used as feed gas. The results are lower than that of 90.8% when DTO reaction was carried out individually, described in section III B. That may result from the existence of more than 10% of H₂ content in the three types of effluent gases after DME synthesis.

At the same time the lifetime of 2%NiSAPO-34/HZSM-5 was prolonged to be more than 5 h due to the diluting component like CO₂ in the effluent gas, which decreased coke formation. The yield of light olefin was 26.1, 77.1, and 84.6 g/m³_{syngas} respectively. The corresponding carbon utilization from biosyngas was 12.7%, 31.4% and 32.8% respectively, which is much higher than that by methanol or direct DME conversion processes.

IV. CONCLUSION

Adding 2%Ni and HZSM-5 to SAPO-34 enhanced the catalytic performance of DTO reaction. The increased catalytic activity of 2%NiSAPO-34/HZSM-5

could ascribe to the coexistence of the small amount of HZSM-5, which owns relatively large pore size and acid sites. Yet the selectivity to light olefin decreased as HZSM-5 was used solely in DTO reaction. The optimized 2%NiSAPO-34/HZSM-5 showed high light olefin yield of 78.0%–90.8% with low CH₄ selectivity (<4%) during 3 h TOS. The maximum C₂= selectivity was obtained at a longer TOS than that of C₃= over the catalysts. It was due to the positive effect of coke deposition with TOS on C₂= formation, which could partly block pores of the catalyst and favor lighter olefin formation on the acid sites. Increasing reaction temperature resulted in the decomposition of DME to CH₄. When the two-stage conversion process was applied for the indirect biosyngas conversion to light olefins via DME, the activity of 2%NiSAPO-34/HZSM-5 was prolonged to be more than 5 h, resulting from the decreased coke formation by the diluting component in the effluent gas from the first-stage DME synthesis reactor. The yield of light olefin was 26.1, 77.16, and 84.6 g/m³_{syngas}, which corresponded to carbon utilization from three types of model biosyngas (H₂/CO/CO₂/N₂/CH₄=33.1/10.8/22.1/27.1/7.05, 40.0/33.8/5.54/15.2/5.57, 41.5/26.9/14.2/14.6/2.89) of 12.7%, 31.4%, and 32.8% respectively. And there is still urgent need for further study on the development of the excellent catalysts and technical processes for light olefin production from biomass.

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.51006110, No.51276183, and No.51036006), the National Natural Research Foundation of China/Japan Science and Technology Agency (No.51161140331), and National Key Basic Research Program 973 Project Founded by MOST of China (No.2013CB228105).

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