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Preparation of Bio-hydrogen and Bio-fuels from Lignocellulosic Biomass Pyrolysis-Oil

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In recent years, production of engine fuels and energy from biomass has drawn much interest. In this work, we conducted a novel integrated process for the preparation of bio-hydrogen and bio-fuels using lignocellulosic biomass pyrolysis-oil (bio-oil). The process includes (i) the production of bio-hydrogen or bio-syngas by the catalytic cracking of bio-oil, (ii) the adjustment of bio-syngas, and (iii) the production of bio-fuels by olefinic polymerization (OP) together with Fischer-Tropsch synthesis (FTS). Under the optimal conditions, the yield of bio-hydrogen was 120.9 g H_2/(kg bio-oil). The yield of hydrocarbon bio-fuels reached 526.1 g/(kg bio-syngas) by the coupling of OP and FTS. The main reaction pathways (or chemical processes) were discussed based on the products observed and the catalyst property.

Key words: Biomass pyrolysis-oil, Bio-hydrogen, Olefins polymerization, Fischer-Tropsch synthesis, Bio-fuels

I. INTRODUCTION

Biomass, as a carbon-containing resource in the earth, has attracted great attention in the world due to its potential applications for producing energy and fuels [1–4]. Lignocellulosic biomass pyrolysis-oil (named as bio-oil) is a black oxygenated organic liquid, which was produced from fast pyrolysis of lignocellulosic biomass. Nowadays, bio-oil has been proved to be an important renewable feedstock for the production of bio-fuels and chemicals [5–7]. As compared with solid biomass, bio-oil can be stored and transported readily, together with the advantage of equipment sharing by using already existent petroleum refining infrastructures. However, the raw bio-oil has high viscosity and acidity, low stability and low heating value due to its high oxygen content. As a result, bio-oil cannot be directly used as engine fuels [8, 9]. Up to now, the upgrading of bio-oil into high grade bio-fuels and chemicals has been widely investigated, especially, the hydrodeoxygenation and the catalytic cracking of bio-oil [8–20]. The bio-oil hydrodeoxygenation can obtain high yield of hydrocarbon bio-fuels. Alternatively, the catalytic cracking of bio-oil seems to be a cheaper route for producing hydrocarbon bio-fuels or chemicals, since such processes are typically operated using cheaper zeolites under the atmospheric pressure, along with free of external hydrogen consumption

[19, 20]. Unfortunately, the upgrading of bio-oil by the hydrodeoxygenation or the catalytic cracking of bio-oil often contains part of oxygenated compounds.

Another important route for the transformation of bio-oil into clean bio-energy is the production of hydrogen for fuel cell applications. The production of hydrogen from bio-oil can be realized by the reforming reactions of oxygenated organic compounds and the water-shift reaction. Various catalysts have been investigated for production of hydrogen via the reforming of bio-oil or its model oxygenates [21–24]. One of the major problems for the catalytic reforming of bio-oil is the deactivation of catalysts due to coke or oligomer deposition even in the presence of an excess of steam. For the production of pure hydrogen from bio-oil, another hindering is that the gas products generally contain a certain amount of methane, carbon monoxide, carbon dioxide, and other gaseous compounds, which increase the difficulty of hydrogen purification and its cost.

Moreover, the catalytic cracking of bio-oil can produce bio-syngas, mainly containing light olefins, CO, CO_2, CH_4, and other gas alkanes [25–27]. This bio-syngas, in general, is able to prepare the liquid hydrocarbon fuels through the olefin oligomerization or Fischer-Tropsch synthesis (FTS). However, the H_2/CO ratio in the bio-oil-derived crude syngas typically is lower than 2, which is required for common requirement for the FTS. A large amount of CO_2 in the crude syngas also reduces the FTS efficiency. Generally, the bio-syngas formed from the catalytic cracking of bio-oil include two types of useful compositions (light olefins and H_2/CO). So far, there are some reports about the

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production of the liquid fuels by FTS and olefinic polymerization alone [28–33]. However, the coupling of FTS and olefinic polymerization seems to improve the yield of the liquid fuels, which has not been investigated as far as we know.

In this work, an integrated catalytic transformation for producing bio-fuels using the bio-oil was demonstrated, which included the catalytic cracking of the bio-oil to bio-hydrogen or bio-syngas, the bio-syngas conditioning, and the synthesis of liquid bio-fuels via the oligomerization of olefins with Fischer-Tropsch synthesis. This integrated catalytic transformation potentially provides a new and useful route for the production of hydrocarbon bio-fuels from lignocellulosic biomass-derived bio-oil.

II. EXPERIMENTS

A. Feedstocks

The crude bio-oil used for this research was obtained by fast pyrolysis in a circulating fluidized bed with a capacity of 120 kg/h of oil in our lab. The bio-oil was produced using rice husk which included 44.12wt% cellulose, 25.74wt% lignin, and 21.93wt% hemicelluloses, along with 44.90wt% C, 6.35wt% H, and 48.30wt% O.

In this work, the light bio-oil with a boiling point of 105−115 °C was used. The chemical compositions, elemental composition, and water content of the light bio-oil used are given in Table I. The use of the light bio-oil can reduce the coke deposition and improve the yield of light olefins during the catalytic cracking of bio-oil, as proved in our previous work [11, 25].

B. Catalyst preparation and characterization

HZSM-5(25) zeolite obtained from Nankai University Catalyst Co., Ltd. (Tianjin, China) was calcined in nitrogen atmosphere at 550 °C for 4 h prior to use. The 5wt%Ce/HZSM-5 catalyst was prepared by impregnation method. A certain amount of HZSM-5 zeolite was impregnated in cerium nitrate solution at room temperature overnight, followed by rotary-evaporation at 60 °C, drying at 80 °C for 6 h, and calcinating at 550 °C for 5 h. The incipient wetness impregnation method was adopted to load the cobalt into the SiO_2 (supplied by Qingdao Haiyang Chem Co., Ltd., China). The details were described elsewhere [34]. The 20wt%Ni/Al_2O_3 catalyst and CuZnAl catalyst (containing 61.2wt% CuO, 33.8wt% ZnO, and 5.0wt% Al_2O_3) were supplied by Jingjiang Co., Ltd. in China. The LTG-0 catalyst was kindly provided by Beijing Huiersanji Green Chem. Co., Ltd., China.

The elemental content in the catalysts was measured by inductively coupled plasma and atomic emission spectroscopy (ICP-AES, Atomscan Advantage, Thermo Jarrell Ash Co., USA). The catalysts were also investigated by NH_3-TPD (temperature programmed desorp-

TABLE I Properties of the bio-oil used[a]. Comp. anal.=composition analysis. Ele. anal.= Elemental analysis.

Comp. anal.	Content/wt%	Ele. anal.	Content/wt%
Acids	26.4	C	42.3
Aldehydes	14.8	H	7.5
Ketones	19.2	O[b]	50.0
Alcohols	4.7	N	0.14
Phenols	2.7	S	<0.1
Furans	9.1		
Non-identified[b]	23.1		

[a] The crude bio-oil was produced by fast pyrolysis of rice husk. The light fraction of the crude bio-oil (named as bio-oil) was used in this work, which was conducted by the distillation of the crude bio-oil from 105−115 °C and 1 atm. The water content in the bio-oil used was 73.1wt%.
[b] By difference.

tion of ammonia), N_2 adsorption/desorption isotherms and X-ray diffraction (XRD). For the NH_3-TPD tests, the catalyst was pretreated at 500 °C under helium flow (ultrahigh purity, 100 mL/min) for 2 h, and adsorption of ammonia was carried out at 120 °C for 1 h. After the catalyst was flushed with He at 120 °C for 1 h, the programmed-desorption of NH_3 was run from 120 °C to 700 °C with a heating rate of 10 °C/min. The catalyst acid strength was obtained by the adsorption-desorption of NH_3, which was detected on-line with a gas chromatograph (GC-SP6890, Shandong Lunan Ruihong Chemical Instrument Co., Ltd., Tengzhou, China). The N_2 adsorption/desorption isotherms of the catalysts were measured at −196 °C using the COULTER SA 3100 analyzer.

The typical NH_3-TPD spectra of Ce/HZSM-5 and LTG-0 catalysts are shown in Fig.1. Two ammonia desorption peaks were observed, assigned to the weak acid sites at 230 °C and the strong acid sites at 450 °C. The ratios of strong to weak acid sites for Ce/HZSM-5 and LTG-0 were 0.79 and 0.93 respectively. As shown in Fig.2, Ce/HZSM-5 and the LTG-0 belong to the ZSM-5 zeolite catalyst. The XRD pattern of 20wt%Ni/Al_2O_3 catalyst present the NiO phase (at 37.5°, 43.3°, and 62.9°) and the Al_2O_3 phase at 2θ=25.4°. The XRD spectrum for CuZnAl indicates that the Cu and Zn element appeared as CuO and ZnO. Co_3O_4 was also observed in Co/SiO_2 catalyst. The main physical and chemical properties of the catalysts are summarized in Table II.

C. Product analysis

1. Production of bio-hydrogen or bio-syngas from bio-oil

For production of bio-syngas from bio-oil, an integrated catalytic transformation process by coupling the

TABLE II Main physical and chemical properties of the catalysts.

Catalyst	Si/Al	$S_{BET}/(m^2/g)$	V_p/nm^3	D_p/nm	Total acid/(μmol NH$_3$/g$_{cat}$)
5wt%Ce/HZSM-5	24±1	285.0±17.2	0.19±0.02	0.5±0.1	335.1±11.9
20wt%NiO/Al$_2$O$_3$	0	102.8±1.2	0.28±0.03	9.7±0.4	136.9±15.3
CuZnAl[a]	0	53.8±0.5	0.18±0.03	13.4±1.1	-
LTG-0	33±1	305.1±26.5	0.16±0.03	0.6±0.1	388.4±20.7
15wt%Co/SiO$_2$	∞	316.4±18.6	0.67±0.03	8.3±1.2	21.7±5.8

Note: Si/Al: the ratio of silicon to aluminum in the zeolites), S_{BET}: Brunauer-Emmett-Teller surface area, V_p: pore volume, D_p: pore diameter.
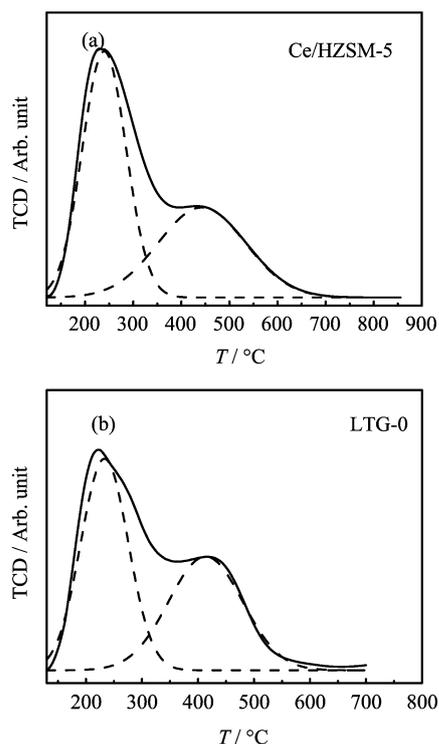[a] CuZnAl: fresh 61.2wt%CuO/33.8wt%ZnO/5.0wt%Al$_2$O$_3$ catalyst.

FIG. 1 Typical NH$_3$-TPD spectra of (a) the fresh Ce/HZSM-5 catalyst and (b) the fresh LTG-0 catalyst.

FIG. 2 Typical XRD spectra of the catalysts.

catalytic cracking reactions, the water gas reaction and the CO$_2$ adsorption were designed and operated under atmospheric pressure. The system consists of three units: one for the production of hydrogen or bio-syngas by the catalytic cracking of the bio-oil, together with the water gas reaction unit for the increase of hydrogen proportion, and the CO$_2$ removal unit via the CO$_2$ adsorbents.

For the catalytic cracking of bio-oil to bio-hydrogen or crude bio-syngas, 10 g of 20wt% Ni/Al$_2$O$_3$ or 5wt% Ce/HZSM-5 catalyst was filled in the catalyst bed, which was held in the reactor by quartz wool. The mixture of bio-oil and water (oil/water mass ratio of about 1:3) was fed into the reactor through a multisyringe pump (TS2-60, Baoding Longer Precision Pump)
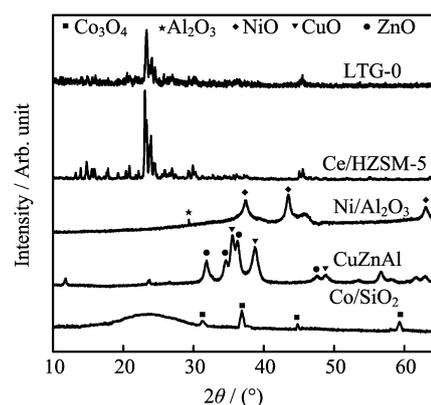
at a given feeding rate. Before each run, the reactor was flushed with nitrogen at a flow rate of 200 cm^3/min for 1 h, and was externally heated to a given temperature by the carborundum heater with a programmed temperature controller. The gaseous products were on-line analyzed using a gas chromatograph (GC-SP6890, Shandong Lunan Ruihong Chemical Instrument Co., Ltd., Tengzhou, China) with two detectors: a TCD (thermal conductivity detector) for analysis of H$_2$, CO, CO$_2$ and CH$_4$ separated on the TDX-01 column, and a FID (flame ionization detector) for gas hydrocarbons separated on the Porapak Q column.

The water gas shift reaction was conducted in the second unit of the reaction system. 3.0 g of the CuZnAl catalyst was typically loaded in the reactor. Before the reaction, the reactor were externally heated to the given temperature. The off-gas of the catalytic cracking process was fed into the WGS reactor. The analysis procedures of the products obtained from the water gas shift reaction unit were the same as the steps for the catalytic cracking, as mentioned above. Then, the CO$_2$ removal by the 15wt% NaOH solution was conducted in the third unit. Typically, 1 L of the 15wt% NaOH solution was loaded in the absorption bottle.
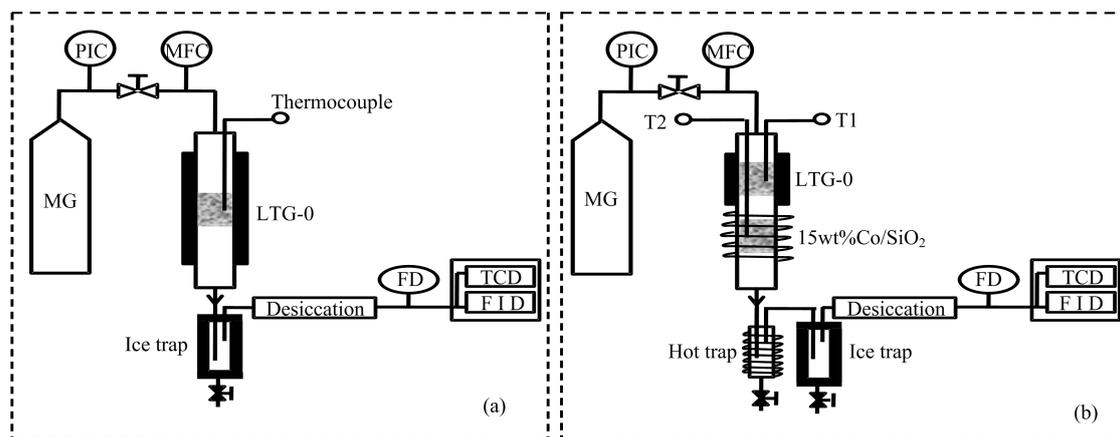
FIG. 3 Schematic diagram of the synthesis of bio-fuels from bio-syngas. (a) the synthesis of bio-fuels by olefinic polymerization or Fischer-Tropsch synthesis, (b) the synthesis of bio-fuels by the coupling of olefinic polymerization and Fischer-Tropsch synthesis. MG=model gas, MFC=mass flow controller, PIC=pressure indicator controller, FD=flow detector, TCD=thermal conductivity detector, FTD= flame ionization detector.

2. Production of hydrocarbon bio-fuels

According to the composition of the adjusted bio-syngas, the model gas with $H_2/CO/C_2H_4/C_3H_6/C_4H_8/N_2$=30.6/14.7/15.0/20.1/4.9/14.7 (in volume ratio) was employed for the production of liquid hydrocarbon fuels. As shown in Fig.3(a), the olefinic polymerization was carried out in a high pressure micro-reactor unit of 10 mm internal diameter, 40 cm in length. 2.0 g of the LTG-0 catalyst was loaded in the center of the reactor. Before the reaction, the reactor was flushed with argon at a flow rate of 200 cm³/min for 30 min, and then was externally heated to the given temperature by the carborundum heaters. The model gas was then fed into the reactor. The reaction conditions were T=300 °C, P=3.0 MPa, and GHSV=1200 h^{-1}. The liquid products were collected in an ice trap immersed in the ice/salt bath, and then analyzed using GC-MS (Thermo Trace DSQ (I)) with a TR-5MS fused-silica capillary column. The stream leaving the ice trap was depressurized and periodically analyzed on line in a gas chromatograph with TCD and FID detectors, as detailed above.

The Fischer-Tropsch synthesis (FTS) was carried out over 2.0 g of the 15wt%Co/SiO₂ catalyst in the same reactor. The system was first purged by an argon flow at the rate of 200 cm³/min for 30 min, followed by pre-reducing stage with a 10%vol H₂/Ar mixture at 400 °C for 8 h, then model gas was fed into the system until reaching the desired pressure by slowly adjusting the system to the desired temperature. The reaction was operated under the following conditions: T=270 °C, P=3.0 MPa, and GHSV=1200 h^{-1}. The liquid products were condensed in two consecutive traps located at the reactor outlet and kept, respectively, at 393 and 268 K. Gas products leaving the ice trap were on-line sampled every 30 min and analyzed using the on-line gas

chromatograph with two detectors, as detailed above. Products collected in the traps were mixed and analyzed using GC-MS (Thermo Trace DSQ (I)) with a TR-5MS fused-silica capillary column.

As shown in Fig.3(b), the olefinic polymerization combined with Fischer-Tropsch synthesis (OP-FTS) reaction was operated in the same stainless tube. Two types of catalysts were loaded in the reactor: 2.0 g of the LTG-0 catalyst in the front part and 2.0 g of the 15wt% Co/SiO₂ catalyst in the back part. The two parts were externally heated by short furnace and heat tape, respectively. The operation steps and the products analysis procedures were the same as that for Fischer-Tropsch synthesis, as mentioned above.

Finally, the conversion, product yield and the resulting product distribution were calculated according to the method reported in Ref.[35–37]. All the tests were repeated three times and the reported data are the mean values of three trials.

III. RESULTS AND DISCUSSION

A. Routes for production of bio-hydrogen and bio-syngas from bio-oil

To produce hydrocarbon bio-fuels from bio-oil, the catalytic transformation of oxygenated organic compounds in bio-oil into hydrogen-containing bio-syngas is required. Thus, we first performed the comparative tests for the catalytic cracking of bio-oil over different characteristic catalysts and the pyrolysis of bio-oil with SiO₂.

As shown in Table III, the gas products produced by the pyrolysis of bio-oil with SiO₂ consist of CO, CO₂, gas alkanes (mainly CH₄), with small amount of desired products of hydrogen and C2=−C4= light olefins. The pyrolysis of bio-oil also formed the organic liquid products (OLPs) mainly including small molecule oxy-

TABLE III Results of different preparation routes of bio-hydrogen and bio-syngas from bio-oil[a].

Routes	Conversion /C-mol%	Yield/(g/kg bio-oil)				Overall carbon yields/C-mol%				
		$C_2^=-C_4^=$	H_2	H_2/CO	Bio-syngas	Gas	C_5^+ oil	Coke/tar	Unrea.[e]	Carbon[f]
Pyrolysis[b]	52.8	23.1	0.6	69.4	92.5	18.7	28.1	10.1	47.2	104.1
CP-I[c]	91.1	Trace	120.9	159.3	159.3	88.3	1.1	0.6	8.9	98.9
CP-II[d]	88.6	239.5	3.1	131.3	370.8	80.1	9.7	2.3	11.4	103.5

	Gas composition/vol%							
	H_2	CO	CO_2	CH_4	C_2-C_4 alkanes	$C_2^=$ alkene	$C_3^=$ alkene	$C_4^=$ alkene
Pyrolysis[b]	5.7	43.6	21.9	13.7	3.1	8.2	2.3	1.5
CP-I[c]	66.0	1.5	31.7	0.8	Trace	Trace	Trace	Trace
CP-II[d]	8.1	24.6	23.5	6.8	2.2	15.3	16.7	2.8

[a] The values are averages of three trials with relative standard deviations <15.1%.
[b] Pyrolysis conditions: T=550 °C, S/C=5.0 and WHSV of 0.4 h^{-1}.
[c] CP-I (catalytic pyrolysis) conditions: T=550 °C, S/C=5.0 and WHSV of 0.4 h^{-1}, 20wt%Ni/Al$_2$O$_3$ catalyst loading (catalyst/bio-oil)=3.
[d] CP-II(catalytic pyrolysis) conditions: T=550 °C, S/C=5.0 and WHSV of 0.4 h^{-1}, 5wt%Ce/HZSM-5 catalyst loading (catalyst/bio-oil)=3.
[e] Unreacted substances.
[f] Carbon balance.

TABLE IV Effect of temperature on the production of bio-syngas by the catalytic pyrolysis of bio-oil under the conditions: 500−650 °C, S/C=5.0 and WHSV of 0.4 h^{-1}.

T/°C	Conversion /C-mol%	Yield/(g/kg bio-oil)			Overall carbon yields/C-mol%				
		$C_2^=-C_4^=$	H_2/CO	Bio-syngas	Gas	C_5^+ oil	Coke/tar	Unreacted	Carbon
500	80.1	187.6	98.5	286.1	65.3	12.1	3.6	19.9	100.9
550	88.6	239.5	131.3	370.8	80.1	9.7	2.3	11.4	103.5
600	93.3	235.9	158.8	394.7	85.0	7.1	2.9	6.8	101.8
650	97.8	224.4	206.1	408.7	90.7	5.6	1.8	4.8	102.9

	Gas composition/vol%							
	H_2	CO	CO_2	CH_4	C_2-C_4 alkanes	$C_2^=$ alkene	$C_3^=$ alkene	$C_4^=$ alkene
500	5.6	23.5	28.8	5.4	3.6	12.4	16.5	4.2
550	8.1	24.6	23.5	6.8	2.2	15.3	16.7	2.8
600	10.2	25.6	26.0	6.3	1.5	15.1	13.2	2.1
650	12.4	28.3	23.3	10.7	0.5	12.1	11.4	1.3

Note: The values are averages of three trials with relative standard deviations <14.2%.

genated organics, which were caused by the thermal decomposition of heavier oxygenated organic compounds in bio-oil.

On the contrary, the catalytic cracking of bio-oil significantly enhanced the bio-oil conversion as well as the yield of the gas products as compared with the pyrolysis of bio-oil. For the catalytic cracking of bio-oil over the 20wt% Ni/Al$_2$O$_3$ catalyst at the typical temperature of 550 °C, the bio-oil conversion reached about 91.1% along with a hydrogen yield of 120.9 (g/kg bio-oil). The gas products was dominant during the catalytic cracking of bio-oil, which mainly included 66.0vol% hydrogen and 31.7vol% carbon dioxide together with trace amount of methane and carbon monoxide. In this sense, the steam reforming of bio-oil reactions and the water gas shift reaction were main reaction pathways, and the Ni-based catalyst like the Ni/Al$_2$O$_3$ catalyst can be employed for the production of bio-hydrogen.

On the other hand, the catalytic cracking of bio-oil over the 5wt%Ce/HZSM-5 catalyst also shows a high bio-oil conversion (about 88.6%). However, the resulting products using 5wt%Ce/HZSM-5 catalyst were quite different from the catalytic conversion of bio-oil with the Ni-based catalyst. The catalytic cracking of bio-oil over Ce/HZSM-5 was mainly converted into H$_2$/CO/CO$_2$ and C$_2$−C$_4$ light olefins over the acidic sites of the zeolite. As shown in Table III, the gas products produced by the catalytic cracking of bio-oil over Ce/HZSM-5 mainly consist of the desired 24.6% CO, 8.1% H$_2$ and light olefins (15.3% C$_2$H$_4$, 16.7% C$_3$H$_6$, 2.8% C$_4$H$_8$), which can be comprehensively utilized as the bio-syngas for the subsequent synthesis of hydro-

TABLE V The gas composition (vol%) of bio-syngas produced by different ways.

Routes	H_2	CO	CO_2	CH_4	$C_2^=$ alkene	$C_3^=$ alkene	$C_4^=$ alkene	C_2-C_4 alkanes
Raw bio-syngas[a]	8.1	24.6	23.5	6.8	15.3	16.7	2.8	2.2
Adjusted syngas-I[b]	19.1	9.7	33.5	7.6	11.3	14.2	2.6	2.0
Adjusted syngas-II[c]	28.7	14.6	trace	11.4	17.0	21.4	3.9	3.0

[a] The raw bio-syngas from catalytic pyrolysis: T=550 °C, S/C=5.0, WHSV=0.4 h^{-1}.
[b] Adjusted syngas-I: the adjusted syngas produced by the low-temperature WGS reaction: T=300 °C, CuZnAl catalyst loading=3.0 g.
[c] Adjusted syngas-II: the bio-syngas after the CO_2 absorption with 15wt% NaOH solution.

carbons bio-fuels.

CO and H_2O.

B. Influence of temperature on the preparation of bio-syngas from bio-oil

Table IV shows the influence of temperature on the preparation of bio-syngas from bio-oil by the catalytic cracking of bio-oil over 5wt%Ce/HZSM-5 catalyst. The conversion of bio-oil increased with increasing temperature, and was close to complete conversion near 650 °C. In the investigated temperature range, the products formed from the catalytic cracking of bio-oil mainly included gas olefins, hydrogen, CO and CO_2, together with small amount of gas alkanes, liquid products (mainly C_6-C_8 aromatics) and coke/tar. The yield of total effective gas (like H_2, CO, C_2-C_4 alkenes) reached 370.8 g/(kg bio-oil) at 550 °C. Further increasing temperature caused an increase of the total effective gas, while a decrease of the light olefins yield due to the increase of gas alkanes (especially methane). The above results indicate that high temperatures will facilitate the deoxygenation of the bio-oil, and at the same time, enhance the deep cracking of the heavier intermediates.

As shown in Table IV, based on the main compounds identified in this work and the previous studies [11, 25], the reaction pathways for the catalytic cracking of bio-oil over an acid molecular sieve catalyst mainly include: (i) the formation of lighter intermediates via breaking the C−C and/or C−O bonds in the oxygenated organic compounds in bio-oil; (ii) the formation of olefin compounds via the deoxygenation (decarboxylation, decarbonylation and dehydration) and catalytic cracking of intermediates; and (iii) formations of low-carbon aromatics by further cyclization and aromatization of light olefins over the acidic sites of the zeolites. Hydrogen should come from the direct decomposition of the oxygenated organic compounds in bio-oil along with the sencond catalytic cracking of intermediates. Gaseous small molecule products (mainly C_2-C_4 light olefins and gas alkanes) were formed by further decomposition of intermediates. The oxygen in the bio-oil was removed by the decarbonylation, decarboxylation and dehydration processes, since oxygenated chemicals observed in the catalytic cracking of bio-oil mainly contain CO_2,

C. Conditioning of bio-syngas by water gas reaction and CO_2 adsorption

To improve the synthesis efficiency of bio-fuels, the conditioning of bio-syngas was conducted by the increase of the H_2/CO ratio and the removal of CO_2. Table V shows the composition distribution of three typical bio-syngas before and after the conditioning of bio-syngas. For the raw bio-syngas from the catalytic pyrolysis of bio-oil at 550 °C over 5wt% Ce/HZSM-5 catalyst, the H_2/CO ratio was very low (about 0.33). To increase the H_2/CO ratio in the bio-syngas, the raw bio-syngas was first adjusted on-line by the low-temperature water gas reaction over the CuZnAl catalyst (named as adjusted syngas-I). The H_2/CO ratio in the adjusted syngas-I was about 1.9, which basically met the requirement of the Fischer-Tropsch synthesis (corresponding to the H_2/CO ratio of 2). However, the content of CO_2 also remarkably increased to 33.5vol% due to the water gas reaction. To increase the effective composition of bio-syngas (H_2, CO, C_2-C_4 alkenes) in the bio-syngas, the adjusted syngas-I was further tuned by the removal of CO_2 with the CO_2 absorption (named as adjusted syngas-II). As can be seen from Table V, the amount of carbon dioxide was reduced near zero (trace), and the final adjusted syngas-II contained 28.7vol% H_2, 14.6vol% CO, 11.4vol% CH_4, 17.0vol% C_2H_4, 21.4vol% C_3H_6, 3.9vol% C_4H_8 and 3.0vol% C_2-C_4 alkanes. The above results indicate that the effective conditioning of bio-syngas was able to simply be realized through the water gas reaction and the CO_2 adsorption.

D. Synthesis of hydrocarbon bio-fuels by olefinic polymerization and Fischer-Tropsch process

Considering that the bio-syngas derived from the catalytic cracking of bio-oil and the conditioning are essentially composed of C_2-C_4 light olefins and H_2/CO, the synthesis of bio-fuel using the adjusted syngas-II was tested by means of three routes: olefinic polymerizations (OP), Fischer-Tropsch synthesis (FTS), OP-FTS process.

TABLE VI Products of different ways to synthesize hydrocarbon bio-fuels.

Products	OP[a]	FTS[b]	OP-FTS[c]
Conversion of gas/C-mol%			
Ethylene	57.6	81.4	88.7
Propylene	87.7	50.3	86.3
Buthylene	84.8	81.9	82.8
Hydrogen	0	83.4	81.6
Carbon	0	61.2	71.2
Distribution[d]/wt%			
C_5	5.6	3.5	4.5
C_6	10.2	10.7	10.2
C_7	12.6	11.2	11.6
C_8	13.5	11.9	13.6
C_9	15.3	12.5	15.3
C_{10}	12.9	14.6	14.1
C_{11}	9.1	8.6	9.3
C_{12}	3.8	5.3	4.2
C_{13}	3.2	4.7	3.1
C_{14}		2.5	0.8
C_{15}		2.4	0.5
C_{15}^+		9.8	2.1
Aromatics			
C_6	0.2		0.2
C_7	0.5		0.4
C_8	3.4		3.1
C_9	3.6		3.2
C_{10}	2.1		1.6
C_{11}	1.2		0.8
C_{12}	0.5		0.2
C_{13}	0.1		0.1
Others	2.1	2.3	1.1
C_8-C_{15}/wt%	69.7	61.5	69.9
Liquid yield	458.2	119.6	526.1

[a] $T=300$ °C, $P=30$ atm, GHSV=1200 h^{-1}, and 2.0 g of LTG-0 catalyst.
[b] $T=270$ °C, $P=30$ atm, GHSV=1200 h^{-1}, and 2.0 g of 15wt% Co-SiO$_2$ catalyst.
[c] T(OP)=300 °C, T(FT)=270 °C, $P=30$ atm, GHSV=1200 h^{-1}, and 2.0 g of LTG-0 catalyst with 2.0 g of 15wt% Co/SiO$_2$ catalyst.
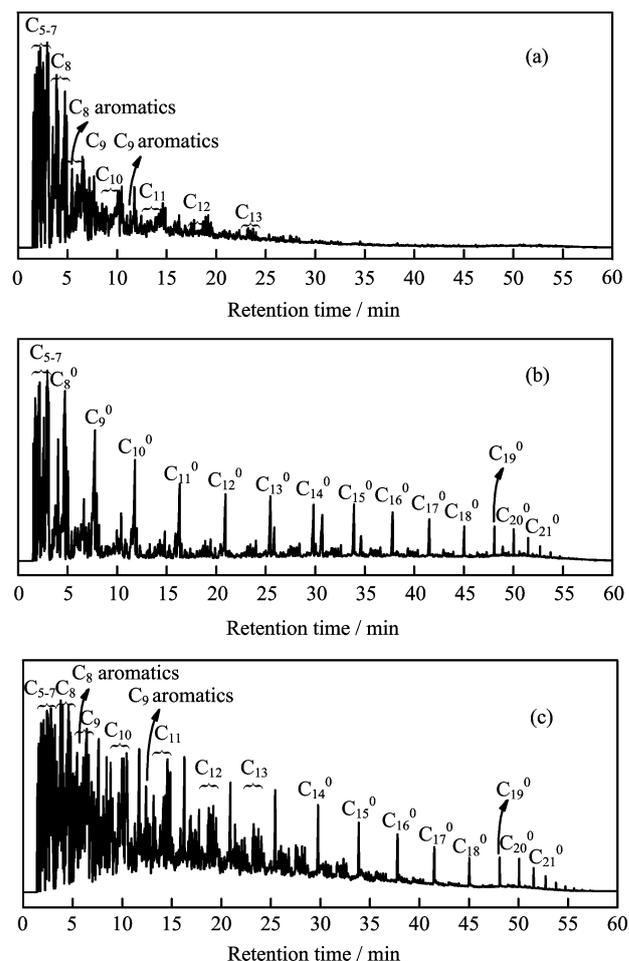[d] Liquid linear hydrocarbons distribution.

FIG. 4 Typical GC-MS spectra (a) the sample from the olefinic polymerization of the bio-oil-derived bio-syngas catalyzed by LTG-0 at 300 °C. (b) the sample from the Fischer-Tropsch synthesis catalyzed by 15wt%Co/SiO$_2$ catalyst. (c) the sample from the olefinic polymerization and Fischer-Tropsch synthesis coupling reaction. Note: C_n means alkenes and alkanes with n carbon atoms, C_n^0 means normal-alkanes with n carbon atoms.

As show in Table VI, the olefinic polymerization over the modified zeolite (LTG-0) can convert the compositions of C_2-C_4 light olefins into liquid hydrocarbon fuels. The main products from the olefinic polymerization mainly included chain hydrocarbons (C_5^+ olefins and C_5^+ paraffins) together with small amount of C_6^+ aromatics. The olefinic polymerization mainly involve the oligomerization of light olefins, the hetero-oligomerization and the cracking of heavier oligomers.

The C_6 olefins were formed by the dimerization of propylene and/or the hetero-oligomerization between ethylene and butenes. The C_8 and C_9 olefins were mainly produced through the dimerization of butenes and the trimerization of propylene respectively. The formation of light odd number alkenes like C_5 and C_7 olefins may originate from the hetero-oligomerization and/or the cracking of heavier oligomers. The paraffins products observed could be formed through the oligomerization of olefins followed by hydrogen transfer, cyclization and isomerization. The C_6^+ aromatic hydrocarbons should be derived from the aromatization of olefins and the hydrogen transfer reactions.

As shown in Table VI, on the other hand, the Fischer-Tropsch synthesis (FTS) over the 15wt% Co/SiO$_2$ catalyst can convert the compositions of H$_2$/CO into liquid hydrocarbon fuels. The main products derived from the
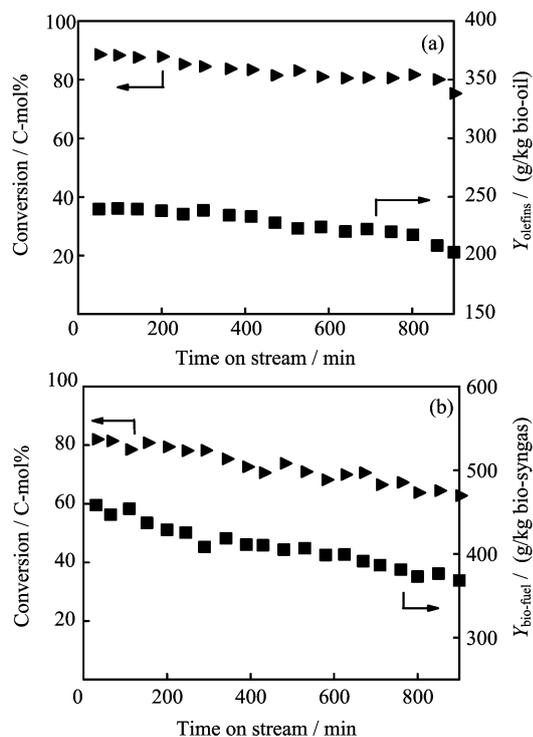
FIG. 5 Catalyst stability during (a) the catalytic cracking of bio-oil to light olefins over the Ce/HZSM-5 catalyst at 550 °C and (b) the synthesis of bio-fuel from bio-syngas over the LTG-0 catalyst at 300 °C.

FTS mainly included chain hydrocarbons (C_5^+ paraffins and C_5^+ olefins). The FTS reaction produces hydrocarbons of variable chain length from a gas mixture of carbon monoxide and hydrogen (bio-oil-derived syngas). The FTS reaction is a building stone (CH_2) by the CO hydrogenation for longer hydro-carbons. The liquid hydrocarbon distributions by FTS depend on the chain growth probability (described as the Anderson-Schulz-Flory (ASF) distribution). As shown in Fig.4, compared with olefinic polymerizations (OP), FTS produced more long-chain hydrocarbons. It was noticed that FTS using the 15wt% Co/SiO$_2$ catalyst can also convert C_2-C_4 light olefins. However, the main products derived from C_2-C_4 light olefins by FTS were C_2-C_4 gas paraffins, which were formed through the hydrogenation of light olefins.

Moreover, the olefinic polymerization combined with Fischer-Tropsch synthesis process (OP-FTS) can convert both C_2-C_4 light olefins and H_2/CO in the bio-syngas. As a result, the yield of the liquid fuels by OP-FTS was obviously higher than the levels from OP or FTS alone. The main products from OP-FTS also included chain hydrocarbons (C_5^+ olefins and C_5^+ paraffins) together with small amounts of C_6^+ aromatics. This suggests that the coupling of olefinic polymerization and Fischer-Tropsch synthesis could be a high efficiency way for the synthesis of bio-fuels with the bio-oil derived bio-syngas.

E. Catalysts stability during transformation of bio-oil to bio-fuels

As shown in Fig.5(a), the stability of Ce/HZSM-5 catalyst during the catalytic cracking of bio-oil was measured by the conversion of bio-oil and the yield of light olefins. After the catalyst was continuously used for 15 h, the conversion of bio-oil and the yields of light olefins were obviously decreased. For the olefinic polymerization step performed at 300 °C, after the LTG-0 catalyst was used for 15 h, the conversion of light olefins degraded by 25%, accompanied with an significantly decrease in the yield of bio-fuel (Fig.5(b)).

IV. CONCLUSION

We studied a novel integrated process for the preparation of bio-hydrogen and bio-fuels using biomass pyrolysis-oil. The Ni-based catalyst was suitable for the production of bio-hydrogen. On the other hand, the catalytic cracking of bio-oil over Ce/HZSM-5 mainly formed the crude bio-syngas containing light olefins and H_2/CO/CO$_2$. The H_2/CO ratio and the efficient composition of bio-syngas were much improved by the water gas reaction and CO$_2$ adsorption. Especially, the yield of the liquid fuels through the coupling of Fischer-Tropsch synthesis and olefinic polymerization was obviously higher than the levels from OP or FTS alone.

V. ACKNOWLEDGMENTS

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