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Catalytic Transformation of Oxygenated Organic Compounds into Pure Hydrogen

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The continual growth in transportation fuels and more strict environmental legislations have led to immense interest in developing green biomass energy. In this work, a proposed catalytic transformation of oxygenated organic compounds (related to bio-oil) into pure hydrogen was designed, involving the catalytic reforming of oxygenated organic compounds to hydrogen-rich mixture gas followed by the conversion of CO to CO_2 via the water gas reaction and the removal of CO_2. The optimization of the different reforming catalyst, the reaction conditions as well as various sources of oxygenated organic compounds were investigated in detail. The production of pure hydrogen, with the H_2 content up to 99.96% and the conversion of 97.1%, was achieved by the integrated catalytic transformation. The reaction pathways were addressed based on the investigation of decomposition, catalytic reforming, and the water gas reaction.

Key words: Oxygenated organic compounds, Hydrogen, Catalytic reforming, Water gas reaction

I. INTRODUCTION

Hydrogen is a clean fuel and has an important role in reducing environmental emissions for the future [1]. Especially, the preparation of pure hydrogen is an attractive subject for fuel cell applications, which are considered to have the potential to provide a clean and alternative energy source for automobile. Hydrogen is also an important raw material for the chemical industry. For instance, it is used for ammonia synthesis, petrochemical refinery and methanol production. The use of lignocellulosic biomass as a rich, environmentally friendly and renewable resource for production of hydrogen or bio-fuels has attracted considerable attention [2–5]. Bio-oil is a black oxygenated organic liquid derived from fast pyrolysis of lignocellulosic biomass, which has been considered to be a promising platform chemical for producing hydrogen, bio-fuels or chemicals [1, 2, 6–9]. However, the raw bio-oil has some unfavorable properties such as high viscosity, high acidity, low stability, and low heating value due to its high oxygen content, which impedes its direct utilization as engine fuels [10]. Thus, it is needed to transform oxygenated compounds in bio-oil into clean fuels to meet the requirements of the conventional transportation fuels. The catalytic re-

forming of bio-oil can produce a rich-hydrogen mixture gas, and further obtain pure hydrogen by gas separation process. Probably, production of hydrogen by the catalytic reforming of bio-oil is one of the most promising options because it can achieve higher yield and higher content of hydrogen, compared with direct gasification of biomass [1, 2].

The bio-oil reforming is mainly determined by the ability of a catalyst to catalyze the reforming reactions of oxygenated organic compounds and the water-shift reaction [1, 2]. Conventional commercial catalysts for the reforming of hydrocarbons are NiO/Al_2O_3 catalyst, usually operating at 700−850 °C [1, 2]. Various modified Ni-based catalysts and noble metal catalysts have been investigated for production of hydrogen via the reforming of bio-oil or its model oxygenates like acetic acid [11–13]. Noble metals generally show higher reforming reaction activity and less carbon depositing than using the Ni-based catalysts, but are not suitable for real applications due to high cost [13]. 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 [1, 2]. 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.

Generally, bio-oil contains hundreds of oxygenated or-

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ganic compounds, including acids, alcohols, aldehydes, ketones, substituted phenolics and other oxygenates coming from the pyrolysis of biomass. In our previous work, much attention has been paid to the production of hydrogen or bio-syngas from bio-oil and its model compounds [14–16]. A low-temperature electrochemical catalytic reforming method for efficient production of hydrogen using the volatile fraction of the bio-oil and its compounds has been investigated [17–21]. An integrated catalytic transformation for production of high pure hydrogen from the bio-oil models was demonstrated, which included the catalytic reforming of oxygenated organic compounds to hydrogen-rich mixture gas followed by the water gas reaction and the removal of CO_2. More attention was paid to production of hydrogen from the model compound of the sugar saccharide due to the lack of invetigation in the past. So far as we know, there is no such report regarding the production of high pure hydrogen from bio-oil and its models with very low contents of CO and CH_4. This integrated catalytic transformation potentially provides a useful route for the production of pure hydrogen from lignocellulosic biomass-derived bio-oil.

II. EXPERIMENTS

A. Catalyst preparation and characterization

The metal and composite metal oxide catalysts with a settled molar ratio were prepared by the side-by-side co-precipitation method using respective metal nitrates as precursors, according to the same procedure introduced in our previous work [18, 19]. Briefly, the preparation mainly included the following steps: (i) the preparation of respective metal nitrates solution, (ii) the preparation of a mixture of NaOH (1 mol/L) and Na_2CO_3 (1 mol/L) as precipitates, (iii) the preparation of precipitates by the side-by-side co-precipitation of respective metal nitrates solution with the precipitators at a constant pH=9.0 and 80 °C, (iv) the precipitates was aged for 12 h at 25 °C, washed until pH=7, and then dried at 110 °C overnight, (v) the precipitates were finally calcined at 550 °C for 6 h to obtain the corresponding metal and composite metal oxide catalysts.

The metallic element contents in the catalysts were determined by inductively coupled plasma and atomic emission spectroscopy (ICP/AES, Atomscan Advantage, Thermo Jarrell Ash Corporation, USA). The catalysts were also characterized by X-ray diffraction (XRD), N_2 adsorption/desorption and temperature programmed oxidation (TPO) analyses, as the same procedures described in our previous work [22–25]. Briefly, the XRD patterns of the catalysts were obtained on an X'pert Pro Philips diffractometer (Philips, Netherlands) using a Cu Kα radiation (λ=0.15418 nm). The Brunauer-Emmett-Teller (BET) surface area and pore volume was determined by the N_2 physisorption

at −196 °C using a COULTER SA 3100 analyzer. The TPO analyses for determining the carbon content deposited on the used catalysts were conducted in a Q5000IR thermogravimetric analyzer (USA). The samples were heated from room temperature to 800 °C with a heating rate of 10 °C /min under the air.

B. Experimental setup and product analysis

As shown in Fig.1, an integrated catalytic transformation process for production of pure hydrogen from the bio-oil model compounds by coupling the catalytic reforming reactions, the water gas reaction and the CO_2 adsorption were designed and operated under atmospheric pressure. The system consisted of three units: one for the production of hydrogen by the catalytic reforming of the bio-oil model compounds (part 1) together with the water gas reaction unit for the conversion of CO to CO_2 (part 2) and the CO_2 removal unit via the CO_2 adsorbents (part 3).

For the production of hydrogen by the catalytic reforming of the bio-oil model compounds, 4 g of the Ni-based catalyst or the composite metal oxide catalyst was typically loaded in the reactor I (inner diameter: 30 mm, length: 400 mm). Before each run, the catalysts were reduced by a 10%H_2/Ar gas at 550 °C for 5 h. Then, the reactor was flushed with nitrogen at a flow rate of 300 cm^3/min for 1 h, and was externally heated to a given temperature by the carborundum heater. The bio-oil model compounds was fed into the reactor I through an inlet pipe (with the inner diameter of 6 mm) by a multisyringe pump (TS2-60, Baoding Longer Precision Pump) at a given feeding rate. 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 moles of all gas products were determined by the normalization method with the standard gas. The collected liquid after the catalytic reforming was weighed to obtain the mass of liquid products. The total carbon contents of the liquid products were measured by a Vario EL III elemental analyzer, and the water content was analyzed by a moisture analyzer (Model ZSD-1, Shanghai, China). The components of the organic liquid were analyzed by GC-MS (Thermo Trace GC/ISQ MS, USA; FID detector with a TR-5 capillary column). The moles of organic liquid were determined by the normalization method with standard samples. The coke deposited on the used catalyst was determined by the TPO analysis.

The water gas shift reaction unit for the conversion of CO to H_2 and CO_2 was conducted in the second unit (named as the second step). Typically, 4 g of the 34wt% CuO/65wt%ZnO/Al_2O_3 catalyst was loaded in the re-
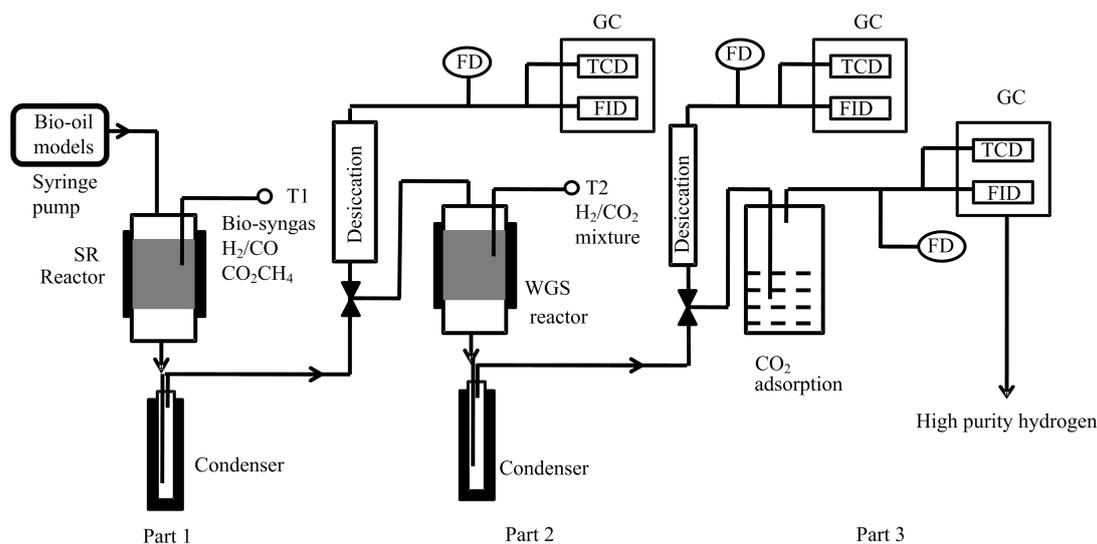
FIG. 1 Schematic diagram of the integrated catalytic transformation system for producing pure hydrogen from the bio-oil model compounds by coupling the catalytic reforming reactions (part 1), the water gas reaction (part 2), and the CO_2 adsorption (part 3).

actor II (inner diameter: 30 mm, length: 400 mm). Before each run, the reactors were externally heated to the given temperatures. Then, the off-gas come from the reactor I was fed into the reactor II. The analysis procedures of the products obtained from the water gas shift reaction unit were the same as the steps for the catalytic reforming, as mentioned above. Finally, the CO_2 removal by the CO_2 adsorbents (like CaO/Na_2CO_3 solution or NaOH solution) was conducted in the third unit. Typically, 1 L of the CO_2 adsorbent solution was loaded in the absorption bottle. The gaseous compositions were on-line analyzed using a gas chromatograph (GC-SP6890, Shandong Lunan Ruihong Chemical Instrument Co., Ltd., Tengzhou, China).

Finally, the conversion, hydrogen yield and the resulting product distribution were calculated according to the method introduced [20, 21]. All the tests were repeated three times and the reported data are the mean values of three trials.

III. RESULTS AND DISCUSSION

A. Screening of reforming catalysts

The choice of the reforming catalysts is crucial in the production of hydrogen processes by the catalytic reforming of oxygenated organic compounds, due to its role in controlling the hydrogen yield and selectivity towards the different products. As shown in Table I, the performance of production hydrogen by the the reforming reaction of glucose over different metals modfied Ni-baesd catalysts was tested under the low-temperature reforming (400 °C) and the high-temperature reforming (700 °C), respicatively. As compared with the common

NiO/Al_2O_3 catalyst, the carbon conversion and the hydrogen yield using the the transition metals or precious metals modfied Ni-baesd catalysts (bimetallic composite oxide catalysts) obviously increased, indicating that adding the transition metals or precious metals into the NiO/Al_2O_3 catalyst improved the low-temperature reforming reactions at 400 °C. Among the tested catalysts, the $20wt\%NiO/20wt\%CoO/Al_2O_3$ catalysts exhibited the highest conversion of glucose along with the highest hydrogen yield. Meanwhile, the bimetallic composite oxide catalysts combined NiO with CoO, CuO or PdO significantly reduced the content of carbon monoxide in the resulting gas products, indicating that adding these transition metals or precious metals enhanced the water gas reaction during the low-temperature reforming process. However, the content of methane kept the close level over different metals modfied Ni-baesd catalysts at 400 °C. This means the methane can not be efficiently removed by the low-temperature reforming reaction.

Futhermore, all tested Ni-baesd catalysts have good reforming activity for the high-temperature reforming of glucose. The content of methane was significantly reduced over different metals modfied Ni-baesd catalysts at 700 °C. However, the content of CO from the high-temperature reforming was increased due to the decrease in the water gas reaction at high reaction temperatures. In view of no significant changes for high-temperature reforming characteristics (the conversion, hydrogen yield, and gas distribution) over the tested catalysts, the NiO/Al_2O_3 catalyst with lower cost was selected as the reforming reaction catalyst for producing pure hydrogen by the following integrated process.

TABLE I Production of hydrogen by the steam reforming of glucose over the different catalysts under the reaction conditions: $T_{SR}=400-700$ °C, WHSV=0.43 h^{-1}, S/C=10 (X: Conversion, Y: H$_2$ relative yield).

Catalyst	$T_{SR}=400$ °C						$T_{SR}=700$ °C					
	X/%	Y/%	Gas distribution/%				Conv./%	Y/%	Gas distribution/%			
			H$_2$	CO	CO$_2$	CH$_4$			H$_2$	CO	CO$_2$	CH$_4$
20wt%NiO/Al$_2$O$_3$	34.0	30.1	62.30	1.21	33.39	3.10	96.6	94.4	66.51	2.76	30.68	0.05
20wt%NiO10wt%PdO/Al$_2$O$_3$	46.5	40.5	63.91	0.24	32.73	3.13	96.1	95.0	66.53	2.63	30.78	0.06
20wt%NiO20wt%CoO/Al$_2$O$_3$	49.1	43.0	64.11	0.12	31.89	3.88	97.6	96.7	66.47	2.94	30.54	0.05
20wt%NiO20wt%CuO/Al$_2$O$_3$	40.3	37.6	63.53	0.81	32.24	3.42	96.3	95.1	66.54	2.59	33.41	0.05
20wt%NiO20wt%Fe$_2$O$_3$/Al$_2$O$_3$	41.5	37.9	62.95	1.02	32.71	3.32	95.8	94.6	66.59	2.57	30.77	0.07

B. Effect of temperature on production of hydrogen by direct catalytic reforming

Although the catalytic reforming of the bio-oil model compounds like acetic acid and ethylene glycol has been much studied [1, 26, 27], the catalytic reforming of sugar molecules is scarcely described in the literature. Figure 2 shows the effect of temperature on the production of hydrogen by the direct catalytic reforming of glucose over the 20wt%NiO/Al$_2$O$_3$ catalyst. The conversion of glucose monotonously rose from 350 °C to 700 °C, and was close to a near complete conversion at 700 °C. The highest yield of hydrogen was about 12.8wt%, corresponding to 95.9% of theoretical yield in the investigated temperature range. The above results indicate that high temperatures will facilitate the catalytic reforming reaction of glucose. Since the catalytic reforming reaction is an endothermic process, and thereby, enhance the yield of hydrogen at higher temperature.

The main gas products derived from the direct catalytic reforming of glucose mainly included H$_2$ and CO$_2$, together with small amount of CO and CH$_4$. The distribution of the products observably depends on the reaction temperature. As the temperatures increased, the content of hydrogen was increased. Especially, the methane content decreased to 0.05% at 700 °C which was caused by the further reforming of the intermediate product of methane. Moreover, it was noticed that the content of carbon monoxide slightly increased with increasing the reforming temperature, accompanied by the decrease in the amount of carbon dioxide. This means that the water gas shift reaction was reduced at higher temperatures.

C. Production of pure hydrogen by coupling reforming reaction, water gas reaction and CO$_2$ removal

To effectively remove carbon monoxide from the reforming-derived gas products, the experimental study on production of pure hydrogen with the integrated process by coupling the reforming reaction, the wa-
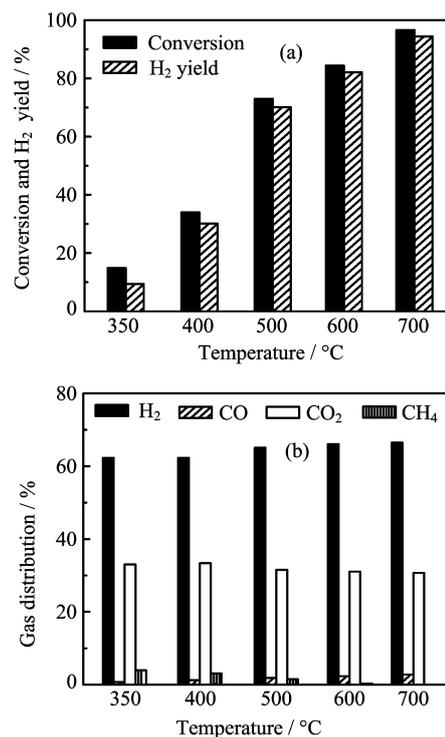

FIG. 2 Effect of temperature on production of hydrogen by direct catalytic reforming of glucose over the 20wt%NiO/Al$_2$O$_3$ catalyst under the reaction conditions: $T_{SR}=350-700$ °C, WHSV=0.43 h^{-1}, S/C=10. (a) Carbon conversion and H$_2$ yield, (b) gaseous products distribution.

ter gas reaction and the removal of CO$_2$ was conducted. Firstly, the catalytic reforming of glucose into CO-containing mixture gas was run in the reactor I over the 20wt%NiO/Al$_2$O$_3$ catalyst, and subsequently, CO obtained in the reactor I were further converted into H$_2$ and CO$_2$ by the water gas reaction over the 34wt%CuO/65wt%ZnO/Al$_2$O$_3$ catalyst in the reactor II in series. Finally, the production of pure hydrogen was conducted by the removal of CO$_2$ by the chemical adsorption method.

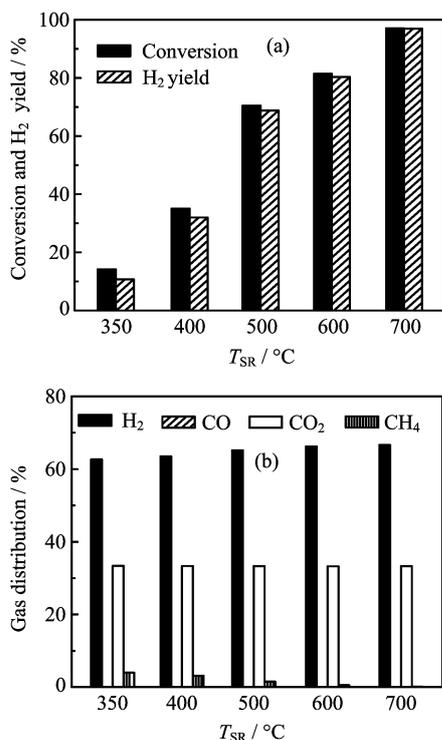Figure 3 shows the effect of the reforming reaction

FIG. 3 Effect of the reforming reaction temperature T_{SR} on the production by coupling the steam reforming of glucose over the 20wt%NiO/Al$_2$O$_3$ catalyst with the water gas shift reaction over 34wt%CuO/65wt%ZnO/Al$_2$O$_3$ catalyst in series. Reaction condition in the reactor I: WHSV=0.43 h^{-1}, S/C=10. Reaction condition in the reactor II: T_{WGS}=250 °C. (a) Carbon conversion and H$_2$ yield, (b) gaseous products distribution.

FIG. 4 Effect of the water gas shift reaction temperature T_{WGS} on the production by coupling the steam reforming of glucose over the 20wt%NiO/Al$_2$O$_3$ catalyst with the water gas shift reaction over 34wt%CuO/65wt%ZnO/Al$_2$O$_3$ catalyst in series. Reaction condition in the reactor I: T_{SR}=650 °C, WHSV=0.43 h^{-1}, S/C=10. (a) Carbon conversion and H$_2$ yield (b) gaseous products distribution.

temperature (T_{SR}) on the production of hydrogen from glucose in the integrated process. The conversion of glucose in the integrated process also showed a positive temperature dependence and their levels were similar to the conversion by the direct catalytic reforming of glucose (Fig.2). This suggests that the conversion of glucose is governed by the properties of the refroming catalysts and the reforming condition. However, the hydrogen yields as well as the gas product distribution derived from the integrated process by coupling reforming reaction with water gas reaction were quite different from the direct catalytic reforming of glucose. Particularly, carbon monoxide was nearly completely eliminated via the water gas reaction in the integrated process (T_{SR}=700 °C and T_{WGS}=250 °C), and the resulting gas composition only contains 69.27% H$_2$ and 30.68% CO$_2$ together with a trace amount of methane (0.05% of CH$_4$). The hydrogen yields obtained in the integrated process were obviously higher than the yields by the direct catalytic reforming, which was attributed to part of hydrogen formed via the water gas reaction.

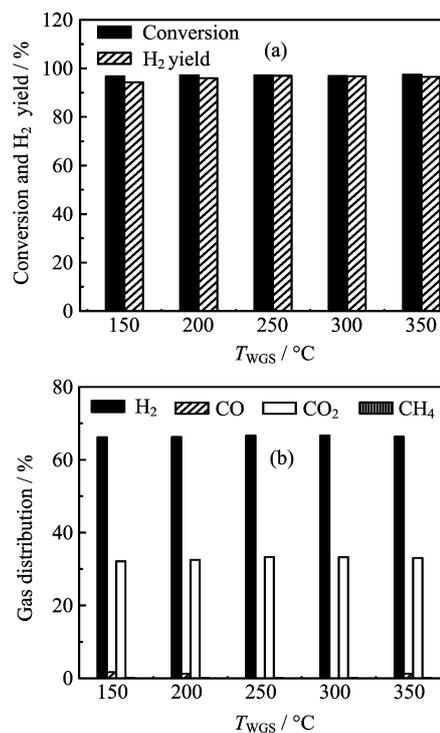To further study the water gas reaction, the reaction temperature in the reactor II was varied in the range of 150−350 °C, while the operating parameters in the reactor I were fixed at the optimal reaction condition. Figure 4 shows the influence of the water gas shift reaction temperature (T_{WGS}) on the production of hydrogen by coupling the steam reforming of glucose with the water gas shift reaction. As increasing the the water gas shift reaction temperature from 150 °C to 350 °C, no evident change of the glucose conversion was observed. The hydrogen yield reached a maximum value of 12.9wt% (close to theoretical value), and carbon monoxide was completely removed via the water gas reaction around 250 °C. Generally, increasing the water gas shift reaction temperature leads to kinetically more favorable for the conversion of CO. However, the water gas shift reaction is exothermic in nature, and thereby, should be thermodynamically favored at a lower temperature. As a result, the water gas shift reaction should be a kinetically and thermodynamically controlled process, leading to a maximum conversion of CO around 250 °C.

In order to prepare high pure hydrogen, we tested the removal of CO$_2$ by the CO$_2$ adsorption method using the different adsorbents. As shown in Table II, 25%(CaO+Na$_2$CO$_3$) solution or 20%NaOH solution behavoirs excellent adsorption ability for carbon dioxide. The CaO and CaOH solution present medium adsorp-
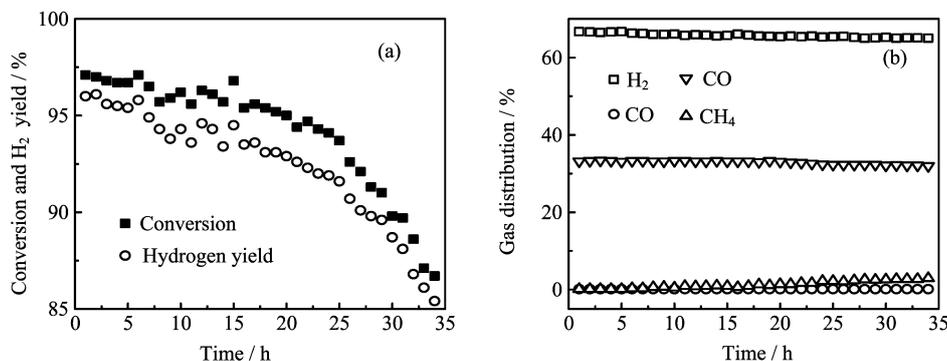
FIG. 5 Catalyst stability during the production of hydrogen from glucose by coupling the steam reforming of glucose over the 20wt%NiO/Al$_2$O$_3$ catalyst with the water gas shift reaction over 34wt%CuO/65wt%ZnO/Al$_2$O$_3$ catalyst in series. Reaction condition in the reactor I: T_{SR}=650 °C, WHSV=0.43 h^{-1}, S/C=10. Reaction condition in the reactor II: T_{WGS}=250 °C. (a) Carbon conversion and H$_2$ yield, (b) gaseous products distribution.

TABLE II Effect (including conversion X and H$_2$ yield Y) of the adsorbents on the production of high pure hydrogen by coupling the steam reforming of glucose over the 20%wtNiO/Al$_2$O$_3$ catalyst with the water gas shift reaction over 34wt%CuO/65wt%ZnO/Al$_2$O$_3$ catalyst in series. Reaction condition in the reactor I: T_{SR}=650 °C, WHSV=0.43 h^{-1}, S/C=10. Reaction condition in the reactor II: T_{WGS}=250 °C.

| Adsorbent | X/% | Y/% | Gas distribution/% | | |
			H$_2$	CO$_2$	CH$_4$
No adsorbent	97.1	13.0	66.65	33.30	0.05
25%CaO	97.1	13.0	85.13	14.82	0.05
25%Ca(OH)$_2$	96.8	12.9	83.24	16.71	0.05
25%(CaO+Na$_2$CO$_3$)	97.0	12.9	99.96		0.04
MCM-41	96.7	12.8	72.82	27.11	0.06
5%NaOH solution	96.8	12.9	75.41	24.53	0.06
10%NaOH solution	97.1	13.0	82.06	17.90	0.04
20%NaOH solution	97.1	13.0	99.95		0.05

TABLE III The BET surface area (S_{BET}), pore volume (V_P), pore diameter (d_P), for the fresh catalyst and the used catalyst after the SR and WGS of the model compounds.

Catalyst	S_{BET}/(m^2/g)	V_P/(cm^3/g)	d_P/nm	Coke/wt%
I^a	115.1	0.28	9.69	-
II^b	106.9	0.26	9.34	0.3
III^c	52.8	0.18	13.4	-
IV^d	52.7	0.17	13.4	-

^{a} Catalyst I: fresh 20wt%NiO/Al$_2$O$_3$ catalyst.
^{b} Catalyst II: used 20wt%NiO/Al$_2$O$_3$ catalyst after the SR reforming of glucose at T_{SR}=650 °C, WHSV=0.43 h^{-1} and S/C=10 for 5 h.
^{c} Catalyst III: fresh 34wt%CuO/65wt%ZnO/Al$_2$O$_3$ catalyst.
^{d} Catalyst IV: used 34wt%CuO/65wt%ZnO/Al$_2$O$_3$ catalyst after the WGS reforming of glucose at T_{WGS}=250 °C for 5 h.

tion capacity for the removal of CO$_2$. But molecular sieves like MCM-41 gives very lower adsorption ability for carbon dioxide. After the CO$_2$ adsorption treatment, 99.96% of high purity hydrogen can be obtained in the integrated process via the coupling of the catalytic reforming reaction, the water gas shift reaction and the CO$_2$ removal in series.

D. Stability of catalysts

As shown in Fig.5, the stability of the catalysts was tested during the production of hydrogen by coupling the reforming reaction and the water gas reaction. The deactivation of the catalysts obviously observed in the above transformation processes, leading to the gradual decrease in the conversion of glucose from 97.1% to

86.7% along with the decrease in the yield of hydrogen from 99.2% to 85.4.0% for 35 h. With increasing the reaction time, the contents of H$_2$ and CO$_2$ decreased, accompanied by the increase of the CO and CH$_4$ compositions.

In the integrated process, two catalysts of 20wt%NiO/Al$_2$O$_3$ and 34wt%CuO/65wt%ZnO/Al$_2$O$_3$, were selected and used for the reforming reaction and water gas reaction, respectively. Table III shows main physical and chemical properties of the fresh and used catalysts. In comparison with the fresh 20wt%NiO/Al$_2$O$_3$ catalyst, the BET surface areas and pore volume for the used ones after the reforming slightly decreased, accompanied with the increase of the Ni particle size. The formation of the coke on the 20wt%NiO/Al$_2$O$_3$ used catalyst was also observed as characterized by the temperature programmed oxidation. Accordingly, the activity decay observed during the the reforming reaction process (in the

TABLE IV Production of hydrogen by the steam reforming of different oxygenated organic compounds over the 20wt%NiO/Al$_2$O$_3$ catalyst under the reaction conditions: WHSV=1 h^{-1}, S/C=4.

Compounds	T_{SR}=400 °C						T_{SR}=700 °C					
	X/%	Y/%	Gas distribution/%				X/%	Y/%	Gas distribution/%			
			H$_2$	CO	CO$_2$	CH$_4$			H$_2$	CO	CO$_2$	CH$_4$
Methanol	91.6	85.8	72.45	0.84	23.49	3.22	99.6	95.8	74.52	4.21	21.22	0.05
Acetone	54.1	50.0	53.13	2.02	29.04	15.81	96.9	90.1	71.80	8.81	19.32	0.07
Formaldehyde	46.7	41.8	60.48	2.11	33.01	4.40	97.2	92.1	66.12	5.30	28.51	0.07
Acetic acid	38.6	34.3	57.42	2.50	29.47	10.61	98.9	92.6	65.73	5.91	28.31	0.05
Glucose	34.0	30.1	60.20	9.01	27.97	2.82	97.1	86.2	66.58	13.10	20.26	0.06
Furan	27.7	25.3	65.38	3.97	28.65	2.06	96.4	90.8	67.65	5.02	27.26	0.07
Phenol	16.9	13.1	58.32	8.81	29.35	3.52	88.3	73.3	64.32	10.67	24.95	0.06

first step) could be attributed to coke deactivation together with irreversible deactivation like the slight decrease in the BET surface areas and the increase of the Ni particle size, caused by the metal nanoparticle aggregation at the higher reforming temperatures. The catalyst deactivation caused by the carbon deposition on the 20wt%NiO/Al$_2$O$_3$ catalyst could be a main factor, since the most of activity (about 94.5%) for the used 20wt%NiO/Al$_2$O$_3$ catalyst was able to be recovered by regenerating the catalyst with oxygen at 600 °C for 5 h.

Moreover, the content of carbon monoxide in the gas products kept at a very low level (<0.1%) for 35 h run. This implies that the 34wt%CuO/65wt%ZnO/Al$_2$O$_3$ catalyst has good stability during the water gas reaction, mainly benefiting from the low-temperature operation conditions. The high stability of the 34wt%CuO/65wt%ZnO/Al$_2$O$_3$ catalyst was also supported by the fact that the negligible coke-deposition and no significant changes in its physical and chemical properties were observed during the water gas reaction.

E. Comparison of production hydrogen from different model compounds

Typically, bio-oil produced through the fast pyrolysis of biomass is a complex mixture of several hundreds of oxygenated organic compounds, which can be classified into acids, alcohols, aldehydes, ketones, sugar saccharide carbohydrates, furans, substituted phenolics and other oxygenates [1, 27]. To gain insight on the differences of the catalytic reforming reactions among different types of compounds, we performed the following comparative experiments using acetic acid, methanol, formaldehyde, acetone, glucose, furan and phenol as the selected model compounds.

Table IV shows the carbon conversion, hydrogen yield and gas product distribution for the catalytic reforming of different feedstocks over the 20wt%NiO/Al$_2$O$_3$

catalyst. The conversion and hydrogen yields obtained from the tested feedstocks were lined up as follows: methanol>acetone>formaldehyde>acetic acid>glucose>furan>phenol. Methanol has the highest low-temperature reforming reactivity for the production of hydrogen, along with a conversion of 91.6% and a H$_2$ yield of 85.8% even at 400 °C. The gas products mainly contains 72.45%H$_2$ and 23.49%CO$_2$ together with the low concentration of CO (0.84%) and CH$_4$ (3.22%). This indicates that the methanol reforming reaction (CH$_3$OH→2H$_2$+CO) and the water gas reaction (CO+H$_2$O→H$_2$+CO$_2$) easily occur under the low-temperature condition. On the contrary, phenol and furan have the lower reforming reactivity at the low-temperature region, corresponding to lower conversion and lower H$_2$ yield less than 30% at 400 °C. Only increasing temperature to 700 °C, the conversions of phenol reached 88.3%. This may be attributed to the high molecular structure stability of aromatic and ring compounds, and thereby, the breaking of the C−C bond in these compounds need to higher reaction temperatures. Glucose also show lower reforming reactivity at the low-temperatures probably due to number of hydrogen bond donors in L-glucose. Moreover, it was noticed that acetone and acetic acid produced higher content of CH$_4$ among the tested compounds. This suggests that the methyl groups can be stripped off from these molecules, then combine with H atom and tranfer to form CH$_4$. Another path for the foamation of CH$_4$ is methanation reacions of CO and/or CO$_2$ with H$_2$ (CH$_3$OH→CO+2H$_2$ and CO+3H$_2$→CH$_4$+H$_2$O).

IV. CONCLUSION

Production of pure hydrogen from oxygenated organic compounds related to bio-oil was proved by a catalytic transformation involving the catalytic reforming of oxygenated organic compounds followed by the conversion of CO to CO$_2$ by the water gas reaction and

the removal of CO_2. The highest content of H_2 up to 99.96% and the conversion of 97.1% were obtained by the integrated catalytic transformation of glucose as the model compound of the sugar saccharides in bio-oil. The chioce of the reforming catalyst, the reaction conditions and various oxygenated organic compounds were investigated. The reaction pathways were discussed based on the observed characteristics of observed characteristics of decomposition catalytic reforming and the water gas reaction. The transformation potentially provides a useful way for production of pure hydrogen using biomass.

V. ACKNOWLEDGMENTS

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