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Hydrogen Production by Low-temperature Steam Reforming of Bio-oil over Ni/HZSM-5 Catalyst

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We investigated high catalytic activity of Ni/HZSM-5 catalysts synthesized by the impregnation method, which was successfully applied for low-temperature steam reforming of bio-oil. The influences of the catalyst composition, reforming temperature and the molar ratio of steam to carbon fed on the stream reforming process of bio-oil over the Ni/HZSM-5 catalysts were investigated in the reforming reactor. The promoting effects of current passing through the catalyst on the bio-oil reforming were also studied using the electrochemical catalytic reforming approach. By comparing Ni/HZSM-5 with commonly used Ni/Al$_2$O$_3$ catalysts, the Ni$_{20}$/ZSM catalyst with Ni-loading content of about 20% on the HZSM-5 support showed the highest catalytic activity. Even at 450 °C, the hydrogen yield of about 90% with a near complete conversion of bio-oil was obtained using the Ni$_{20}$/ZSM catalyst. It was found that the performance of the bio-oil reforming was remarkably enhanced by the HZSM-5 supporter and the current through the catalyst. The features of the Ni/HZSM-5 catalysts were also investigated via X-ray diffraction, inductively coupled plasma and atomic emission spectroscopy, hydrogen temperature-programmed reduction, and Brunauer-Emmett-Teller methods.

Key words: Bio-oil, Hydrogen, Steam reforming, Ni/HZSM-5 catalyst

I. INTRODUCTION

Hydrogen is considered to be clean fuel and could play an important role in reducing environmental pollution for the future. Especially, its production is an attractive subject of current interest for fuel cell applications [1−3], which are considered to have the potential to provide a clean energy source for automobile as an alternative to gasoline or diesel engines. The use of renewable biomass as a new feedstock for hydrogen production or energy source has attracted considerable attention in recent years [4−6], because it is not only be environmentally friendly but also would open new opportunities for utilization of renewable resources, which are globally available.

Steam reforming of pyrolysis oil (bio-oil) is one of the promising routes of hydrogen production from renewable sources. Bio-oil, generated mainly from biomass via fast pyrolysis process [7], generally contains numerous and complex oxygenated organic compounds [8]. The bio-oil can be further reformed via steam over reforming catalyst in order to obtain high content of hydrogen. In view of higher yield of hydrogen, production
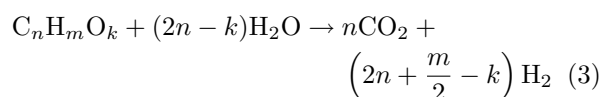
of hydrogen through the reforming of bio-oil may be one of the most promising options in various routes proposed for biomass conversion into hydrogen [6]. Generally, the steam reforming of bio-oil is simplified as the steam reforming of the oxygenated organic compound ($C_nH_mO_k$) by the following steam reforming reaction: [9]:

$$C_nH_mO_k + (n-k)H_2O \rightarrow nCO + \left(n + \frac{m}{2} - k\right)H_2 \quad (1)$$
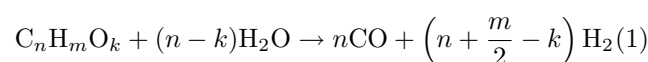
The above reaction is followed by the water-gas shift reaction (WGS reaction):

$$nCO + nH_2O \rightarrow nCO_2 + nH_2 \quad (2)$$
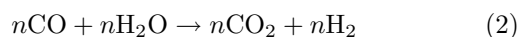
Therefore, the overall process can be represented:

$$C_nH_mO_k + (2n-k)H_2O \rightarrow nCO_2 + \left(2n + \frac{m}{2} - k\right)H_2 \quad (3)$$

The steam reforming of bio-oil proceeds according to the reforming reactions of $C_nH_mO_k$ in bio-oil with water and the further WGS reaction.

For the catalytic steam reforming of bio-oil [10−14], it has been widely explored via the reforming catalysts including the oxide catalysts, the Ni-based catalysts, and the noble metal-loaded catalysts *etc.* Lower reforming temperature is essential from the viewpoint of economy.

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Noble metals (Pt, Ru, Rh) are generally more effective than the Ni-based catalysts and less carbon depositing [15, 16]. Such catalysts are not common in real applications because of their high cost. Another hindering 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 (molar steam-to-carbon ratio S/C>5) [17]. Thus, it is very significant to realize low temperature reforming of bio-oil using non-noble metal catalysts. It is also important to decrease carbon deposits during the bio-oil reforming process.

Zeolites are an important class of crystalline aluminosilicates, which have been widely used in heterogeneous catalysis because of their well-defined pore structures and capabilities of extremely high surface area and surface acidity. The zeolite HZSM-5 is a versatile material that has been used for a variety of heterogeneous catalytic reactions, including catalytic cracking and NO_x-selective catalytic reduction [18−20]. It is generally accepted that the zeolite HZSM-5 shows good catalytic performance in the reaction of dehydrogenation and C-C rupture. And HZSM-5 is also effective for hydrogen production from C_7H_{14} reforming, cellulose gasification, dimethyl ether reforming *etc.* [21−23].

In this work, a series of Ni/HZSM-5 catalysts synthesized by the impregnation method were successfully applied for production of hydrogen from low-temperature steam reforming of bio-oil. The influences of catalyst composition and reaction parameters (reforming temperature T, S/C and current I) were investigated in detail. The performance of the bio-oil reforming was remarkably enhanced by the HZSM-5 support and the electrochemical catalytic reforming method. The features of the Ni/HZSM-5 catalysts were also investigated using X-ray diffraction (XRD), the inductively coupled plasma and atomic emission spectroscopy (ICP/AES), hydrogen temperature-programmed reduction (H_2-TPR), and Brunauer-Emmett-Teller.

II. EXPERIMENTS

A. Catalyst preparation and catalyst characteristic

Nickel catalysts supported on HZSM-5 (Si/Al=25) and Al_2O_3 were prepared by the impregnation method using nickel nitrate as the metal precursor. $Ni(NO_3)_2$ was dissolved in water and HZSM-5/Al_2O_3 was added to the solution under continuous stirring. The slurry was dried at 110 °C for 24 h and then calcined in air at 500 °C for 5 h for complete decomposition of nickel nitrate. This series of catalysts were defined as Ni_x/ZSM (x=the weight percent of NiO in the samples, and ZSM is the HZSM-5 support).

XRD of the catalysts was measured on an X'pert Pro Philips diffractometer with a Cu Kα radiation. The BET surface area, pore volume and pore diameter were determined by the N_2 physisorption at −196 °C using

TABLE I Some chemical properties including elemental composition (%) for the crude (21%H_2O) and pretreated (39.3%H_2O) bio-oils derived from the sawdust.

Bio-oil	C	H	O	Chemical formula
Crude	54.5	6.7	38.7	$CH_{1.48}O_{0.53}\cdot0.32H_2O$
Pretreated	48.5	8.5	43.3	$CH_{2.03}O_{0.67}\cdot0.89H_2O$

an ASAP 2020 M+C analyzer. The H_2-TPR tests were performed for studying the reduction features of the catalysts. Before the run, the sample was treated in the flow argon (30 mL/min) for 1 h. Then, the sample was subsequently contacted with a flow reduction gas (10% H_2 in argon, 40 mL/min) and heated from 100 °C to 750 °C at a constant rate of 10 °C/min.

B. Bio-oil and reaction system

Bio-oil was produced by the fast pyrolysis of biomass in a circulating fluidized bed with a capacity of 120 kg/h of oil in our Lab (patent: ZL01263584.7, the Anhui Province Key Laboratory of the Biomass Clean Energy). The chemical formula was represented as $CH_{2.03}O_{0.67}\cdot0.89H_2O$ (Table I) for the pretreated bio-oil derived from the sawdust.

The experiments were carried out in the continuous flow systems, using a quartz fixed-bed reactor under atmospheric pressure. The experiment setup and measurement were described in our previous work [24, 25]. The mixture of bio-oil and water with different S/C was fed into a forewarmer using the multi-syringe pump (TS2-60), and then the mixture was preheated at 200 °C before passing through the catalyst bed in the reactor. The reforming experiments were performed with the following two modes, *i.e.*, the common steam reforming (CSR) mode and the electrochemical catalytic reforming (ECR) mode. For the CSR mode, the catalyst bed was homogeneously heated by an outside furnace. In the case of ECR mode, an annular Ni-Cr wire, which passed through a given ac current, entwined around a quartz column for heating the catalyst and synchronously providing the electrons onto the catalyst, and installed in the center of the reactor. The catalyst was uniformly embedded around the Ni-Cr wire. The products were analyzed by two on-line gas chromatographs using TDX-01 and Porapark Q columns.

The hydrogen yield was calculated as a percentage of the stoichiometric potential, the carbon conversion was calculated by the total mol carbon in the gaseous products divided by the mol carbon in the fed bio-oil. The carbon selectivity was defined as the mol carbon in per product divided by the total mol carbon which has been converted in the fed bio-oil [26−28].
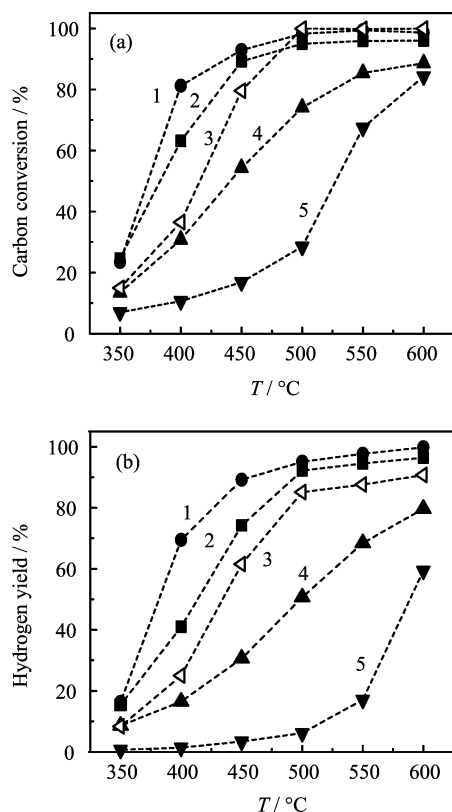
FIG. 1 Influence of the reaction temperature on (a) the carbon conversion and (b) the hydrogen yield for steam reforming of bio-oil over different Ni-based catalysts. Reforming conditions: S/C=17, GHSV=6000 h^{-1} and P=101 kPa. 1. Ni$_{20}$/ZSM, 2. Ni$_{30}$/ZSM, 3. Ni$_{20}$/Al$_2$O$_3$, 4. Ni$_{10}$/ZSM, 5. Ni$_{15}$/ZSM,

III. RESULTS AND DISCUSSION

A. Comparison of catalytic activities over different Ni-based catalysts

The reforming performances of bio-oil over various catalysts, including Ni$_5$/ZSM, Ni$_{10}$/ZSM, Ni$_{20}$/ZSM, Ni$_{30}$/ZSM, and Ni$_{20}$/Al$_2$O$_3$, were tested as a function of reforming temperature (350−600 °C) at a given S/C=17 and a gas hourly space velocity (GHSV=6000 h^{-1}) under about 101 kPa. Figure 1 presents the carbon conversion and hydrogen yield versus temperature over the above catalysts. As shown in Fig.1(a), the Ni$_5$/ZSM catalyst with adding a small amount of Ni presents a very poor activity for the steam reforming of inorganic compounds in the bio-oil. With the addition of Ni increasing from 5% to 20% on the HZSM-5 support, the conversion of carbon in the reforming of bio-oil is significantly improved, indicating that the Ni element is the most important active site. However, superfluous Ni over 20% impregnated HZSM-5 is not conducive to enhance the carbon conversion. The carbon conversion over all Ni-based cat-
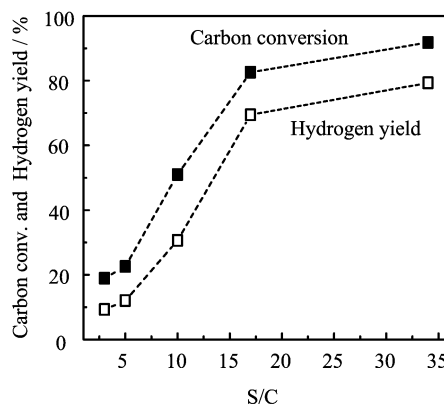

FIG. 2 Effect of the S/C on the carbon conversion and the hydrogen yield for steam reforming of bio-oil over the Ni$_{20}$/ZSM catalyst. Reforming conditions: T=400 °C, GHSV=6000 h^{-1} and P=101 kPa.

alysts increased with increasing the reforming temperature in our investigated range. The Ni$_{20}$/ZSM catalyst has higher catalytic activity than the other tested ones. In particular, the carbon conversion over the Ni$_{20}$/ZSM catalyst is obviously higher compared with the behavior of the common Ni/Al$_2$O$_3$ catalyst below 500 °C. This means that the supporter also plays an important role in the bio-oil reforming over the Ni-based catalysts. As shown in Fig.1(b), the hydrogen yield versus temperature over the above catalysts has a similar trend with the carbon conversion versus temperature. The H$_2$ yield over the Ni$_{20}$/ZSM catalyst ranged from 16.4% to 99.8% in our investigated temperature range (350−600 °C), which was significantly higher than the values over the Al$_2$O$_3$-supported Ni catalyst (Ni$_{20}$/Al$_2$O$_3$). Thus, much attention in this work was paid to study the hydrogen production from the steam reforming of inorganic compounds in the bio-oil over the Ni$_{20}$/ZSM catalyst.

B. Effects of S/C and current on the steam reforming of the bio-oil

In this work, the influences of the most important parameters except T, i.e., S/C and I on the reforming process of the bio-oil over the Ni$_{20}$/ZSM catalyst were investigated in detail using the stream as the carrier gas in the reforming reactor. The steam used as a carrier gas has several advantages. (i) it serves as a required reactant in the reforming process of the bio-oil, (ii) it can decrease the formation of coke and tar in the bio-oil reforming process, and (iii) it can simplify the purification procedure of the reforming products in comparison with inner gases such as N$_2$ as carrier gas. On the other hand, the content of water contained in the crude bio-oil was about 21.0%. After the pretreatment by vaporizing the crude bio-oil from 60 °C to 180 °C, the amount of
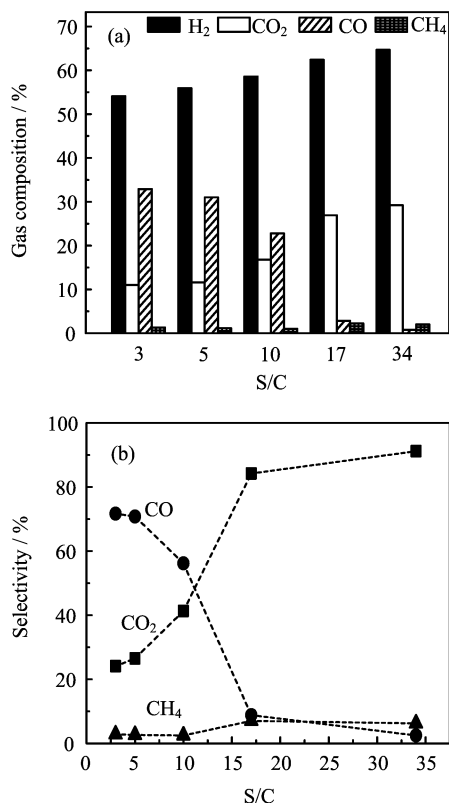

FIG. 4 Effect of the current on the carbon conversion and the hydrogen yield for steam reforming of bio-oil over the Ni_{20}/ZSM catalyst. Reforming conditions: $T=400$ °C, S/C=17, GHSV=6000 h^{-1} and $P=101$ kPa.

FIG. 3 Effect of the S/C on (a) the gas product composition and (b) the carbon selectivity for steam reforming of bio-oil over the Ni_{20}/ZSM catalyst. Reforming conditions: $T=400$ °C, S/C=17, GHSV=6000 h^{-1}, and $P=101$ kPa.

the water contained in the treated bio-oil increased to about 39.3% (Table I). When we calculated the S/C, both the content of water in the pretreated bio-oil and that of the additional water supplemented were taken into account.

Figures 2 and 3 show the influences of S/C on the hydrogen yield, the carbon conversion, the distribution and carbon selectivity of the reforming products, respectively. Both the hydrogen yield and the carbon conversion were obviously enhanced by the S/C ratio. The intent of the bio-oil steam reforming process is to make as much hydrogen as possible by the reforming reactions of the oxygenated organic compounds in the bio-oil in the presence of steam over a catalyst. It has been revealed that the reaction pathways occurred in the bio-oil steam reforming process is very complex (*e.g.*, the reforming reactions between various inorganic compounds and water, secondary cracking of the inorganic compounds, reforming reactions of the fragments as well as the water-gas shift reaction *etc.*) [6] and a lot of potential products may form, depending on the catalysts and reforming conditions used. The reforming reaction (Eq.(1)) is generally endothermic and is favored by high temperature, leading to a higher carbon conversion and higher H_2 yield at higher temperature. In contrast, the
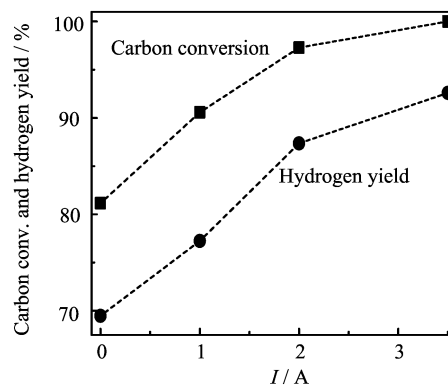
water-gas shift reaction (Eq.(2)) is exothermic and favors lower temperature. The increase of stream amount is in favor of both the reforming reaction and the water-gas shift reaction, resulting in the increase of the hydrogen yield at higher S/C. Moreover, present results show that H_2 and CO_2 are the major products in the bio-oil's steam reforming over the Ni_{20}/ZSM together with some amount of CO and CH_4 in the effluent gaseous compounds. The proper S/C is 17.0, and too high S/C could noticeably reduce the efficient utilization rate of bio-oil and energy in unit time.

As shown in Fig.3, the dry gas composition varies with the S/C ratio. Typical composition of the resulting gas at $T=400$ °C, S/C=17 and GHSV=6000 h^{-1} contained 62.4% H_2, 2.82% CO, 26.9% CO_2, 2.25% CH_4. With increasing the S/C ratio from 3.0 to 34.0 at 400 °C, the content of H_2 in the dry gas products increases from about 54.1% to 64.7%, and the content of CO_2 has a similar trend from about 11.0% to 29.2%, but the content of CO decreases from about 32.9% to 0.8%, indicating that the products derived from the steam reforming of the bio-oil are the H_2/CO_2-rich mixture gas. Apart from the H_2, CO_2, and CO products, only a small amount of CH_4 in the range of 1.01%−2.25 % was also detected. In order to more clearly reveal the feature of the composition distribution from the steam reforming of the bio-oil, the carbon selectivity of gas products were depicted as a function of S/C at $T=400$ °C and GHSV=6000 h^{-1} (Fig.3(b)). The above results indicate that a higher S/C ratio favors shifting in the water-gas shift equilibrium to form CO_2 [29, 30].

Besides S/C ratio, it was also observed that the behavior of the bio-oil reforming was very sensitive to I passing through the catalyst, which was described as the ECR [24, 28]. Figure 4 presents the influence of current on the carbon conversion and the hydrogen over the Ni_{20}/ZSM catalyst at the fixed conditions of $T=400$ °C, S/C=17, GHSV=6000 h^{-1}, and $P=101$ kPa.
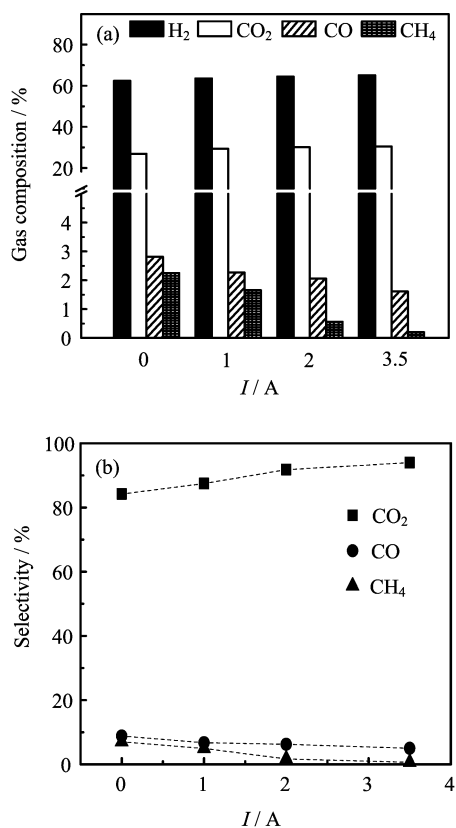
FIG. 5 Effect of the current on (a) the gas product composition and (b) the carbon selectivity for steam reforming of bio-oil over the Ni_{20}/ZSM catalyst. Reforming conditions: T=400 °C, S/C=17, GHSV=6000 h^{-1}, and P=101 kPa.

TABLE II The BET surface area (S_{BET}), pore volume (V_P), pore diameter (D_P) for the fresh catalysts.

Samples	S_{BET}^{a}/(m^2/g)	$V_P^{a,b}$/(cm^3/g)	$D_P^{a,c}$/nm
HZSM-5	263.6	0.10	5.50
Ni_{20}/Al_2O_3	118.5	0.32	7.80
Ni_{20}/ZSM	184.3	0.18	5.18

[a] Evaluated from the N_2 adsorption-desorption isotherms.
[b] BJH desorption cumulative volume of pores between 17.000 and 3000.000 Å diameter.
[c] BJH desorption average pore diameter (4 V/A).

were higher than those in CSR. Even though temperature in the center of the catalyst bed was almost close to the average value in the catalyst bed in our investigated range (350−600 °C), the local temperature on the surface of the electrified Ni-Cr wire or near the wire, generally, was obviously higher than the averaged temperature. Accordingly, the activity of the catalyst reforming near the electrified Ni-Cr wire should be significantly higher than other position in the bed, partly, leading to the enhancement of the apparent overlap reforming effect. On the other hand, the enhancement of the decomposition and reforming in the ECR process may be partly caused by the thermal electrons. The presence of the thermal electrons both on the electrified Ni-Cr wire and on the electrified catalyst surface was observed by the anionic TOF measurements [28, 31]. It is well known that when an electrified metal or a metal oxide is heated, electrons can boil off its surface, leading to thermal emission of electrons from surface (*i.e.*, thermal electron emission) [32]. It has been reported that thermal electrons on a metal or a metal oxide surface play an important role in the reduction process (*e.g.*, $O_2+4e^-\rightarrow 2O^{2-}$) [33], the dissociation and reforming of ethanol or acetic acid [34]. Thus, the thermal electrons may partly contribute to the decomposition and reforming of the bio-oil, leading to the increase of the hydrogen yield in the ECR process. Moreover, it was also found that the energy efficiency in the ECR reforming process was higher than that in the CSR process, which may be explained by the multiple roles including local temperature effect, the effect of thermal electrons, and less heat loss in the inner heating mode. Further work is still required to clearly understand the reforming mechanism in the ECR process.

C. Basic physical and chemical properties of catalysts

Some basic physical and chemical properties for the fresh catalyst and the used one after reforming of bio-oil with and without current applied to the catalyst were characterized using BET, TPR, and XRD techniques.

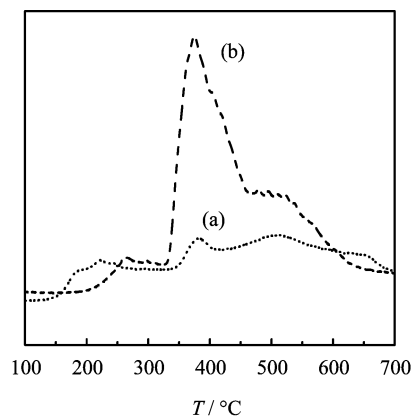The BET surface areas (S_{BET}), pore volume (V_P), and pore diameter (D_P) for the fresh catalysts were

Both the carbon conversion and the hydrogen yield were significantly enhanced by the current through the catalyst. With increasing the current from 0 A to 3.5 A, the yield of hydrogen increased from 69.5% to 92.6% and the carbon conversion rose from 81.2% to 100%. In addition, it was found that the content of H_2 and CO_2 in the reforming products increased with increasing the current, accompanied by the decrease of the CO and CH_4 content (Fig.5). For example, the concentration of hydrogen increased from 62.4% to 65.1% with increasing the current from 0 A to 3.5 A at 400 °C, while the content of methane decreased from 2.25% to 0.2%. The products selectivity in the reforming processes of bio-oil was mainly determined by the steam reforming reactions of the oxygenated organic compounds in the bio-oil and their cracking fragments, the dissociation of the compounds as well as the water-shift reaction. The decrease of the CH_4 content in the products at high current may reflect the thermal electrons from the Ni-Cr wire promoted the steam reforming and dissociation of hydrocarbons [27].

It was noticed that the ECR mode and the CSR mode had different temperature distribution in the catalyst bed [31]. The maximal temperature gradients in ECR

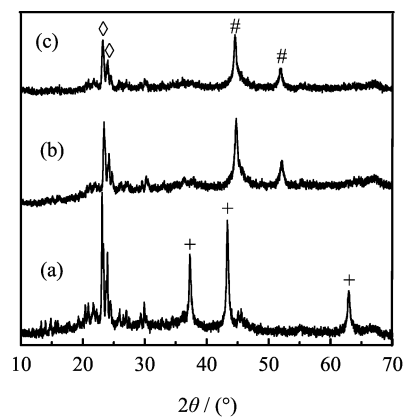FIG. 6 H_2-TPR profiles (a) Ni_5/ZSM and (b) Ni_{20}/ZSM.

FIG. 7 Typical XRD spectra for (a) the fresh Ni_{20}/ZSM catalyst, (b) the used Ni_{20}/ZSM catalyst after steam reforming of bio-oil for 6 h, and (c) the used Ni_{20}/ZSM catalyst after steam reforming of bio-oil for 4 h (conditions: I=3.5 A, T=400 °C, S/C=17, GHSV=6000 h^{-1}, and P=101 kPa). "+" NiO, "♯" Ni, and "◇" HZSM-5.

summarized in Table II. When the HZSM-5 support was impregnated with 20%NiO, the BET surface area obviously decreased from 263.6 m^2/g to 184.3 m^2/g, accompanied by an increase of the V_P from 0.10 cm^3/g to 0.18 cm^3/g. This shows that some interaction between Ni species and HZSM-5 support has occurred during the catalyst preparation process.

The reduction behavior and interaction between NiO and HZSM-5 support in the Ni/ZSM catalysts were investigated by the TPR analyses (Fig.6). The reduction of Ni_{20}/ZSM catalyst presents three H_2 consumption peaks, a weak peak near 260 °C, a strong asymmetric profile at around 375 °C and a small shoulder at 500 °C, respectively corresponding to free NiO with very small microcrystal size on the surface of catalysts, bulk NiO, and NiO bonded to HZSM-5 support whose interaction results in increasing the reduction temperature of this NiO. Compared with the reduction profile of Ni/Al_2O_3 catalyst [35, 36], the maximum reduction peak of Ni/ZSM significantly shifts to the lower temperature, which implies the interaction of NiO with the Al_2O_3 is much stronger than that with the HZSM-5. That different interaction maybe lead to different catalytic performance on Ni_{20}/ZSM and Ni_{20}/Al_2O_3 in the steam reforming of bio-oil, and proper intensity of interaction between NiO and HZSM-5 supports not strong interaction which could be favorable to the improvement of catalytic activity.

Figure 7 shows typical XRD spectra of three samples. For the fresh catalyst (Fig.7(a)), the main characteristic peaks are identified as the diffractions of NiO phase (37.3°, 43.3°, and 62.9°) and HZSM-5 phase (23.1° and 23.9°), respectively corresponding to JCPDS 89-5881 and JCPDS 80-0922. Beside the diffraction peaks of HZSM-5, it was also observed new peaks appearing at 2θ=44.6° and 52.0° in Fig.7 (b) and (c), which were attributed to the diffraction structure of the metal Ni phase. This indicates that, after the CSR and ECR of the bio-oil, part of NiO was reduced into the metallic Ni (*i.e.*, NiO+H_2→Ni^0+H_2O, where H_2 was produced by

the reforming of bio-oil.). It is noticed that the diffraction peaks of NiO phase almost disappeared after reduction by H_2, which may be ascribed to relatively weak interaction between NiO and HZSM-5 support compared with Ni/Al_2O_3 [35, 36].

IV. CONCLUSION

The Ni_{20}/ZSM catalyst containing 20%NiO in the catalyst using the HZSM-5 support was prepared by the impregnation method and successfully applied for the low-temperature reforming of the organic compounds in bio-oil. The influences of the most important parameters, the reforming temperature (T), the molar ratio of steam to carbon fed (S/C), and the current (I) on the reforming process of the bio-oil over the Ni_{20}/ZSM catalyst were investigated. Both the carbon conversion and the hydrogen yield were significantly enhanced by the reforming temperature, the S/C ratio, and the current through the catalyst. The hydrogen yield of 92.6% with a bio-oil conversion near 100% reached at T=400 °C, I=3.5 A, S/C=17, GHSV=6000 h^{-1}, and P=101 kPa. The good performance in low-temperature reforming of the oxygenated organic compounds in bio-oil may mainly attribute to promotion of the HZSM-5 supporter in the Ni/ZSM catalyst together with the effect of thermal electrons. Potentially, it may be a useful candidate to produce hydrogen from bio-oil.

V. ACKNOWLEDGMENTS

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