

## ARTICLE

# Production of Hydrogen from Bio-oil Using Low-temperature Electrochemical Catalytic Reforming Approach over CoZnAl Catalyst

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High-efficient production of hydrogen from bio-oil was performed by electrochemical catalytic reforming method over the CoZnAl catalyst. The influence of current on the hydrogen yield, carbon conversion, and products distribution were investigated. Both the hydrogen yield and carbon conversion were remarkably enhanced by the current through the catalyst, reaching hydrogen yield of 70% and carbon conversion of 85% at a lower reforming temperature of 500 °C. The influence of current on the properties of the CoZnAl catalyst was also characterized by X-ray diffraction, X-ray photoelectron spectroscopy, thermal gravimetric analysis, and Brunauer-Emmett-Teller measurements. The thermal electrons would play an important role in promoting the reforming reactions of the oxygenated-organic compounds in the bio-oil.

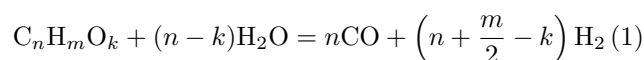
**Key words:** Hydrogen, Bio-oil, CoZnAl catalyst, Electrochemical catalytic reforming

## I. INTRODUCTION

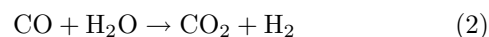
Hydrogen is considered to be clean fuel and could play an important role in reducing environmental emissions in the future [1–3]. Unlike the fossil fuels, hydrogen burns cleanly, without emitting any environmental pollutants. In addition, hydrogen possesses the highest energy content per unit of weight (about 120.7 kJ/g), compared with any other known fuels. Hydrogen is also an important raw material for the chemical industry, which is mainly used for ammonia synthesis. Currently, most of the commercial hydrogen is primarily produced from steam reforming of methane (nature gas), ethanol and other hydrocarbons such as naphtha, heavy residues from petrochemical processes *etc.* [2–4]. The use of lignocellulosic biomass as a new feedstock for hydrogen production has attracted considerable attention in recent years [5–7], because it is not only environmentally friendly but also would open new opportunities for utilization of renewable resources.

Bio-oil, generated from biomass via fast pyrolysis process [8–14], generally, contains numerous complex oxygenated organic compounds, which include acids, alcohols, aldehydes, ketones, and substituted phenolics *etc.* The route of the steam reforming of bio-oil involves fast pyrolysis of biomass to generate bio-oil, and then reforms the bio-oil to produce a gaseous rich-hydrogen mixture. Probably, bio-oil reforming is one of the most

promising options because it can achieve higher yield of hydrogen. The bio-oil reforming would be mainly determined by the ability of a catalyst, which plays an important part in the steam reforming reactions, to help to decompose the oxygenated organic compounds ( $C_nH_mO_k$ ) in bio-oil



and in the water-shift reaction [15]



In the case of the high temperature reforming of bio-oil, partial thermal decomposition of bio-oil and the Boudouard reaction ( $2CO=CO_2+C$ ) may simultaneously occur [16–18].

Various catalysts, including the oxide catalysts, the Ni-based catalysts, and noble metal-loaded catalysts *etc.*, have been selected and used for producing hydrogen via the steam reforming of bio-oil or model oxygenated compounds (*e.g.*, acetic acid, ethylene glycol) [19–41]. Conventional steam reforming catalysts for the steam reforming of hydrocarbons contain 10%–33% NiO on a mineral support (*e.g.*, alumina, magnesia), and are operated at  $T=600\text{--}850$  °C and  $S/C=5\text{--}13$ . Lower reforming temperature is essential in the eye of green-energy. Haga *et al.* had widely studied the catalytic reforming behavior of Ti, Zr, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sb, Ru, Pt, or Rh supported on  $Al_2O_3$  for ethanol steam reforming [42]. They concluded that Co/ $Al_2O_3$  catalyst showed the better selectivity of the hydrogen production from the ethanol reforming [42]. The Co-based catalysts with different supporters such as ZnO,

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SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> have also been investigated in the steam reforming of ethanol or bio-ethanol [43–46]. The Co/Al<sub>2</sub>O<sub>3</sub> catalyst seems to possess higher activity in the reforming of ethanol and water-gas shift reactions [46].

In our previous work, much attention has been paid to the fast pyrolysis of biomass [47–48], production of hydrogen or bio-syngas from the volatile fraction of the bio-oil and its model compounds [49–54], and the liquid bio-fuels synthesis such as gasoline and diesel *etc.* [51]. Recently, we have explored a novel electrochemical catalytic reforming (ECR) method for efficient hydrogen producing from the bio-oil, using the Ni-based catalysts [52–54]. In this work, we studied the behavior of the bio-oil electrochemical catalytic reforming using the CoZnAl catalyst, which would be useful in increasing the hydrogen yield, reducing the operating temperature and depressing the catalyst inactivation.

## II. EXPERIMENTS

### A. Catalyst preparation and characterization

The CoZnAl catalysts with a settled molar ratio, were prepared by the side-by-side co-precipitation method at a constant pH, and using respective metal nitrates as precursors and Na<sub>2</sub>CO<sub>3</sub> (1 mol/L) as precipitates. The main preparation procedures including: (i) preparation of respective metal nitrates solution, (ii) preparation of Na<sub>2</sub>CO<sub>3</sub> (1 mol/L) as precipitates, (iii) preparation of precipitates by the side-by-side co-precipitation of respective metal nitrates solution with the precipitators at a constant pH=8.0±0.5 and 80 °C, (iv) the precipitates was aged for 10 h at 25 °C, and then pumped and washed until pH=7, and dried overnight in an oven at 110 °C; (v) heated the precipitates at the rate of 1 °C/min in air to 450 °C and calcined at 450 °C for 5 h to obtain the corresponding mixture-oxides catalysts; (vi) the mixture-oxides catalysts were crushed into 0.1–0.2 mm for the reforming tests.

The metallic contents in the prepared catalysts were measured by inductively coupled plasma and atomic emission spectroscopy (ICP/AES, Atom scan Advantage of Thermo Jarrell Ash Corporation, USA). XRD measurements were employed to investigate the diffraction structure changes of the catalysts. X-ray diffraction patterns of the catalysts were recorded on an X'pert Pro Philips diffractometer using a Cu K $\alpha$  radiation. The surface elements and their states were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed on an ESCALAB-250 (Thermo-VG Scientific, USA) spectrometer with Al K $\alpha$  (1486.6 eV) irradiation source. The C1s peak at 284.6 eV was generally used as a calibration standard for determining the peaks' position and the elemental concentration. The Brunauer-Emmett-Teller (BET) surface area and pore volume was determined by the N<sub>2</sub>

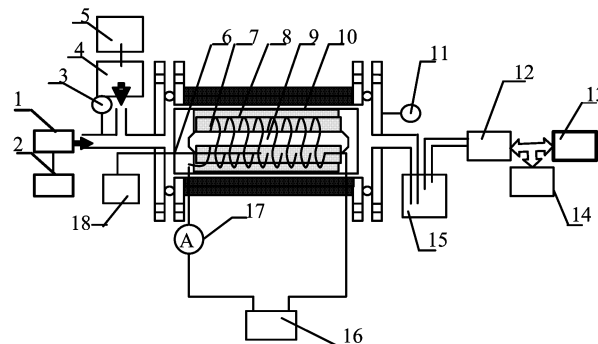


FIG. 1 Schematic setup of the fixed-bed flow quartz-reactor system for the electrochemical catalytic reforming of bio-oil. 1: Steam generator, 2: steam flow controller, 3 and 11: nanometer, 4: micro-injection pump, 5: oil tank, 6: thermocouple, 7: Ni-Cr alloy wire, 8: catalyst, 9: inside quartz tube, 10: outside heater, 12: dryer, 13: gas chromatograph (GC1), 14: gas chromatograph (GC2), 15: ice trapper, 16: ac power supply, 17: ampere-meter, 18: temperature programmed controller.

physisorption at  $-196$  °C using a COULTER SA 3100 analyzer.

### B. Bio-oil and reaction system

Bio-oil was produced by the fast pyrolysis of sawdust in a circulating fluidized bed with a capacity of 120 kg/h of oil at our lab. The crude oil is a dark-brown organic liquid and contains different products, such as hydroxy-aldehydes, hydroxyketones, sugars, carboxylic acids, phenolics, and so forth. Some of them are nonvolatile materials, and easily form carbon depositions onto the catalyst surface. This would lead to the fast deactivation of catalysts. In this work, the volatile organic components in the crude bio-oil, which were distilled with the temperature from 80 °C to 180 °C, were used for the reforming experiments. These volatile components were about 50%–60% in the crude oil. As the main elemental compositions of the vaped oil were C, H, and O, we can represent it as a chemical formula of CH<sub>2.03</sub>O<sub>0.67</sub>·0.89H<sub>2</sub>O [55].

As shown in Fig.1, the bio-oil steam reforming experiments were carried out in the continuous flow systems, using a quartz fixed-bed reactor under atmospheric pressure. The bio-oil was fed into the reactors using the multi-syringe pump (model: TS2-60, Baoding Longer Precision Pump), the steam from a steam-generator was simultaneously fed into the reactors for adjusting the S/C ratio (molar ratio of steam to carbon in bio-oil fed). The steam amount was controlled by the mass flow controller, and the effluent gases from the reactors were measured by flow display. Temperature and its distributions were measured by the thermocouples, which were inserted into the catalyst beds. We performed the reforming experiments with the following two modes,

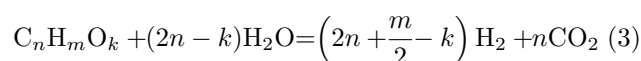
TABLE I Typical temperature distribution in the catalyst bed for the CSR and ECR modes at 101 kPa.

Modes	$f_{\text{total}}/(\text{mL}/\text{min})$	$I_{\text{inside}}/\text{A}$	Position	$T/^\circ\text{C}$	$T_{\text{average}}/^\circ\text{C}$
CSR	0	0	(0, 0)	552	551.4
			(25 mm, 0)	551	
			(-25 mm, 0)	550	
			(0, 1.5 mm)	553	
			(0, -1.5 mm)	551	
CSR	30	0	(0, 0)	550	551.0
			(25 mm, 0)	556	
			(-25 mm, 0)	547	
			(0, 1.5 mm)	553	
			(0, -1.5 mm)	549	
CSR	300	0	(0, 0)	549	549.2
			(25 mm, 0)	555	
			(-25 mm, 0)	543	
			(0, 1.5 mm)	552	
			(0, -1.5 mm)	547	
ECR	0	2	(0, 0)	551	550.8
			(25 mm, 0)	548	
			(-25 mm, 0)	548	
			(0, 1.5 mm)	544	
			(0, -1.5 mm)	563	
ECR	30	2	(0, 0)	554	553.6
			(25 mm, 0)	557	
			(-25 mm, 0)	547	
			(0, 1.5 mm)	545	
			(0, -1.5 mm)	565	
ECR	300	2	(0, 0)	551	550.0
			(25 mm, 0)	556	
			(-25 mm, 0)	542	
			(0, 1.5 mm)	538	
			(0, -1.5 mm)	563	

the common steam reforming (CSR) mode and the electrochemical catalytic reforming (ECR) mode. For the ECR mode, an annular Ni-Cr wire, which was passed through a given ac electronic current, entwined around a quartz column and installed in the center of the reactor. It could heat the catalyst and synchronously provided the electrons onto the catalyst. The catalyst was uniformly embedded around the Ni-Cr wire. To make a certain reforming temperature, the catalyst bed was heated by a supplementary outside furnace. For the CSR mode, ac current was shut off and the catalyst bed was homogeneously heated by an outside furnace. Temperature distributions in the catalyst bed under different conditions were first measured by the thermocouples before running reforming test (Table I). The temperature in the center of the catalyst bed, generally, is almost close to the average value in our investigated range (400–600 °C). Generally, the averaged temperature in the catalyst bed was approximately used as the

reaction temperature in the ECR and CSR reforming experiments.

The products of the reforming reactions were analyzed by two on-line gas chromatographs (GC1 and GC2) with thermal conductivity detector (TCD). The hydrogen yield was calculated as a percentage of the stoichiometric potential, in case of complete conversion of carbon element in the bio-oil to  $\text{CO}_2$  according to the following reaction



The potential yield of hydrogen is  $(2n+m/2-k)$  mole per mole of carbon in the feed. The carbon conversion was calculated by the total molar carbon in the gaseous products divided by the molar carbon in the fed bio-oil. Generally, all experiments were repeated three times. The difference for each repeating, in general, ranged from zero to about 10%.

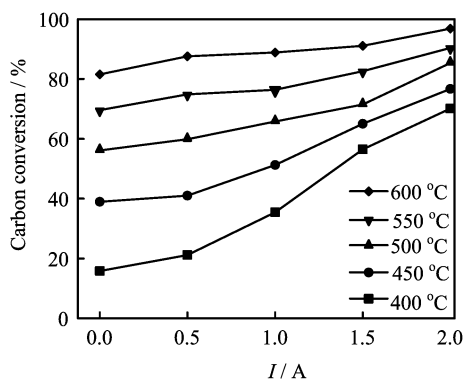


FIG. 2 Effect of current  $I$  on the carbon conversion measured as a function of current through the CoZnAl catalyst at different fixed temperature. Reforming conditions:  $S/C=6.6$ ,  $GHSV=6200\text{ h}^{-1}$ , and  $P=101\text{ kPa}$ .

### III. RESULTS AND DISCUSSION

#### A. Effect of current on reforming of bio-oil over CoZnAl catalyst

The performance of the bio-oil electrochemical catalytic reforming over the CoZnAl catalysts was tested in a continuous flow fixed-bed quartz reactor. Based on the screening tests of the catalyst, the CoZnAl catalyst with an optimal Co:Zn:Al molar ratio near 1.2:1.0:3.0 was used in this study. The CoZnAl catalyst has a particle size of 0.18–0.25 mm. The BET surface area and pore volume was about  $115.9\text{ m}^2/\text{g}$  and  $0.26\text{ cm}^3/\text{g}$ . Beside the temperature effect, it was observed interestingly that the behavior of the bio-oil reforming was also very sensitive to the current  $I$  through the CoZnAl catalyst, which was described as the ECR mode. To investigate the influence of current on the bio-oil reforming, we performed tests under different current, with other experimental conditions (*i.e.*, temperature  $T$ ,  $S/C$ , and gas hourly space velocity ( $GHSV$ )) being maintained.

Figure 2 shows the dependence of the carbon conversion on current  $I$  under the different fixed reforming temperature of 400, 450, 500, 550, and 600 °C, respectively, with  $S/C=6.6$  and  $GHSV=6200\text{ h}^{-1}$ . In the CSR mode, the carbon conversion was only 15.8% at 400 °C. When the current was added to the CoZnAl catalyst (*i.e.*, the ECR mode), the carbon conversion was remarkably enhanced, particularly at lower temperature range (400–500 °C). It was found that the carbon conversion increased from 15.8% to 70.1% with the increasing of current from 0 to 2 A at 400 °C, and reached 90.3% at  $I=2\text{ A}$  and  $T=550\text{ °C}$ . In addition, the hydrogen yield also increased with the increasing of current (Fig.3). For the CSR mode, the hydrogen yield was very low (about 10.3%) under the reforming condition of  $T=400\text{ °C}$ ,  $S/C=6.6$ , and  $GHSV=6200\text{ h}^{-1}$ . When the current was added to 2 A, however, the hydrogen yield increased to 48.1% at the same temperature of 400 °C,

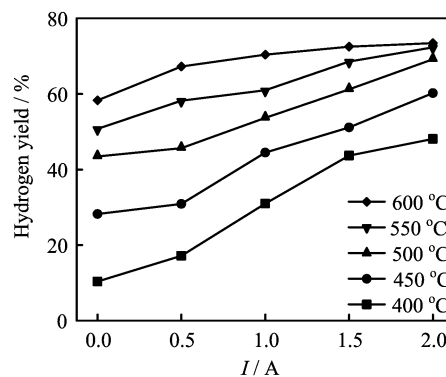


FIG. 3 Effect of the current  $I$  on the hydrogen yield over the CoZnAl catalyst at different temperature. Reforming conditions:  $S/C=6.6$ ,  $GHSV=6200\text{ h}^{-1}$ , and  $P=101\text{ kPa}$ .

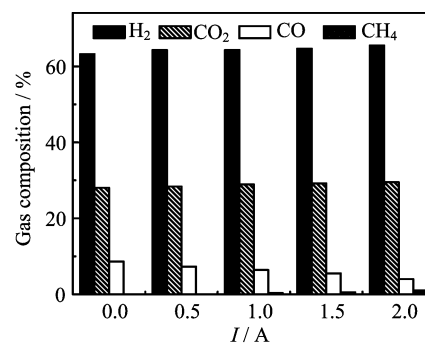


FIG. 4 Influence of the current  $I$  on the gaseous product compositions over the CoZnAl catalyst. The gaseous product compositions from left to right at different current are  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$ , respectively. Reforming conditions:  $T=450\text{ °C}$ ,  $S/C=6.6$ ,  $GHSV=6200\text{ h}^{-1}$ , and  $P=101\text{ kPa}$ .

and reached 70.0% at  $I=2\text{ A}$  and  $T=500\text{ °C}$ . Figure 4 depicts the influence of the current on typical composition of the gaseous products over the CoZnAl catalyst (reforming condition:  $I=0\text{--}2\text{ A}$ ,  $T=450\text{ °C}$ ,  $S/C=6.6$ ,  $GHSV=6200\text{ h}^{-1}$ , and  $P=101\text{ kPa}$ ). Hydrogen was the major product (63%–66%), and also with small amount of  $\text{CO}_2$  (28%–30%) and  $\text{CO}$  (4%–9%) in our investigated range. A trace amount of  $\text{CH}_4$  (<1%) was also observed in the effluent carbonaceous compounds. It was found that the concentrations of  $\text{H}_2$  slightly increased with the increasing of current. The above results indicate that the low-temperature reforming (400–500 °C) of bio-oil can be achieved by the electrochemical catalytic reforming approach and using the CoZnAl catalyst.

Moreover, the stability of the CoZnAl catalyst for the conventional CSR and ECR mode of bio-oil were also tested by measuring the carbon conversion as function of the time on stream. Figure 5(a) shows typical curve for the carbon conversion measured at  $T=550\text{ °C}$ ,  $S/C=7.0$ ,  $GHSV=6200\text{ h}^{-1}$  in the CSR mode. No obvious change of the carbon conversion was observed in the initial 5 h. A gradual decrease of the catalytic ac-

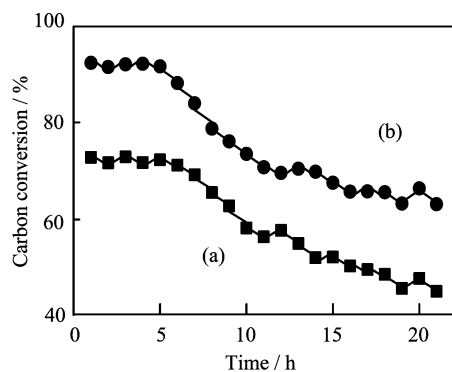


FIG. 5 The stability of the CoZnAl catalyst for the bio-oil reforming in CSR and ECR. Reforming conditions: (a) CSR:  $I=0$  A,  $T=550$  °C,  $S/C=7.0$ ,  $GHSV=6200$  h<sup>-1</sup>, and  $P=101$  kPa, (b) ECR:  $I=2.0$  A,  $T=550$  °C,  $S/C=7.0$ ,  $GHSV=6200$  h<sup>-1</sup>, and  $P=101$  kPa.

tivity was observed for a longer term test. For example, the carbon conversion gradually decreases from about 70% to 45% for 20 h reforming. A similar trend of the catalyst deactivation was observed for ECR mode of bio-oil. Generally, the catalyst deactivation occurring in the reforming process of the bio-oil, mainly be caused by the deposition of carbon (coke-formation) on the catalyst surface [44, 49]. We further estimated the amount of the carbon deposition by the TGA measurements. After the 22 h reforming, the amounts of the carbon deposition were about 16.1% for the ECR mode and 12.9% for the CSR mode.

## B. Influence of current on catalyst properties

The influence of current on the properties of the CoZnAl catalyst was further characterized by XRD and XPS measurements. Figure 6 shows the XRD spectra of four samples: the fresh CoZnAl catalyst, the used CoZnAl catalyst after the CSR reforming of bio-oil for 5 h, the used CoZnAl catalyst after the ECR reforming of bio-oil for 5 h, and the treated CoZnAl catalyst via a current passing through the catalyst under the argon ambience for 10 h, respectively. For the fresh catalyst (Fig.6(a)), some broad diffraction peaks were observed at  $2\theta=31^\circ$ ,  $37^\circ$ ,  $45^\circ$ ,  $56^\circ$ ,  $59^\circ$ , and  $65^\circ$ , which were mainly attributed to  $Co_3O_4$  [44], together with  $CoAl_2O_4$  and  $ZnAl_2O_4$  [44]. However, the XRD patterns for the used catalyst after the CSR and ECR reforming are quite different from that of the fresh one. As shown in Fig.6 (b) and (c), the ZnO, CoO, and Co phases appeared for the used ones after reforming. This means that the oxide states in the fresh catalyst were partly reduced during the bio-oil reforming process. The reduction of the oxide states was mainly attributed to the reduction process by hydrogen, which was formed in the reforming of bio-oil *e.g.*,  $Co^{3+}+H_2\rightarrow Co^{2+}$ . Especially, the reduction from the oxidation state to the

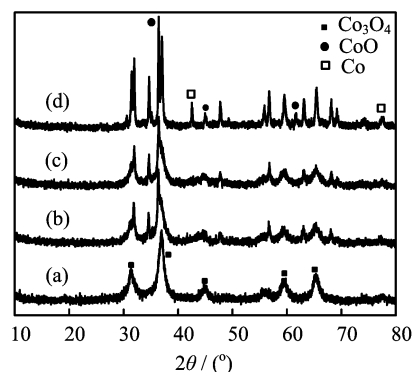


FIG. 6 XRD spectra of four samples (a) the fresh CoZnAl catalyst, (b) the used CoZnAl catalyst after the CSR reforming of bio-oil for 5 h ( $T=600$  °C,  $S/C=7.0$ ,  $GHSV=6200$  h<sup>-1</sup>, and  $P=101$  kPa); (c) the used CoZnAl catalyst after the ECR reforming of bio-oil for 5 h ( $I=2.0$ A,  $T=600$  °C,  $S/C=7.0$ ,  $GHSV=6200$  h<sup>-1</sup>, and  $P=101$  kPa); (d) the treated CoZnAl catalyst via a current passing through the catalyst under the argon ambience for 10 h (treatment conditions:  $I=2.2$  A,  $T=600$  °C,  $GHSV=6200$  h<sup>-1</sup>, and  $P(Ar)=101$  kPa), respectively.

lower oxide states or the metallic phase also occurred when a current passed through the catalyst under the argon or helium ambience (Fig. 6(d)). One of possible explanation is that a part of the oxide states were reduced by the thermal electrons (*e.g.*,  $Co^{3+}+3e^-\rightarrow Co^0$ ) when a current passed through the catalyst. This explanation was supported by the previous experimental observation that the desorption of the thermal electrons from the electrified catalyst was directly observed by the TOF measurements [52, 53].

Moreover, the alterations of the atomic states on the catalyst surface after the CSR or ECR reforming were further investigated by the XPS measurements. As shown in Fig.7(a), the bind energies at about 780.4 and 795.5 eV were observed for the pristine catalyst, which were assigned to the main line of  $Co^{3+}(2p_{3/2})$  and its satellite respectively [45]. After the CSR or ECR reforming (Fig.7 (b) and (c)), the main line in the Co XPS spectrum was obviously shifted to 780.0 eV, corresponding to the change from  $Co^{3+}(2p_{3/2})$  to  $Co^{2+}(2p_{3/2})$ . The shift from higher bind energy to the lower one was also observed when a current passed through the catalyst under the argon or helium ambience (Fig.7(d)).

Figure 8 shows the Zn XPS spectra for four samples: the pristine CoZnAl catalyst, the used ones after the CSR of bio-oil for 5 h, the used ones after the ECR of bio-oil for 5 h, and the treated catalyst via a current passing through the catalyst under the argon ambience for 10 h, respectively. For the pristine catalyst (Fig.8(a)), the bind energy of  $Zn^{2+}$  at about 1022.25 eV was assigned to the main line of  $Zn^{2+}(2p_{3/2})$  [56]. After the CSR and ECR reforming (Fig.8 (b) and (c)), the binding energy shifted to 1021.75 and 1021.45 eV

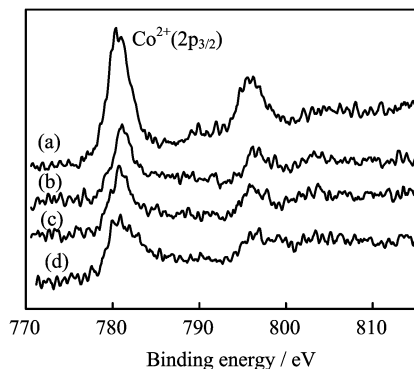


FIG. 7 Co XPS spectra for (a) fresh CoZnAl catalyst, (b) the used CoZnAl catalyst after the CSR for 5 h (reforming conditions:  $I=0$  A,  $T=600$  °C,  $S/C=7.0$ ,  $GHSV=6200$  h<sup>-1</sup>, and  $P=101$  kPa), (c) the used CoZnAl catalyst after the ECR reforming for 5 h, reforming conditions:  $I=2.0$  A,  $T=600$  °C,  $S/C=7.0$ ,  $GHSV=6200$  h<sup>-1</sup>, and  $P=101$  kPa, and (d) the treated CoZnAl catalyst via a current passing through the catalyst under the argon ambience for 10 h (treatment conditions:  $I=2.2$  A,  $T=600$  °C,  $GHSV=6200$  h<sup>-1</sup>, and  $P(\text{Ar})=101$  kPa), respectively.

respectively. After treating the catalyst in the argon ambience via a current passing through the catalyst for 10 h (Fig.8(d)), the bind energy of Zn<sup>2+</sup> decreased to 1021.40 eV. The shift of the bind energy may reflect that part of ZnAl<sub>2</sub>O<sub>4</sub> changes to the ZnO phase when the current passed through the catalyst. The above results clearly showed that Co was in +3 “formal” oxidation states in the fresh catalyst prepared and part of Co<sup>3+</sup> (*i.e.*, the Co<sub>3</sub>O<sub>4</sub> phase) was reduced to Co<sup>2+</sup> (*i.e.*, the CoO phase) and/or metallic Co<sup>0</sup> when the current passed through the catalyst.

### C. Explanation of current effect on bio-oil reforming

Present results show that the performance of the bio-oil reforming is significantly promoted by the current through the catalyst during the ECR process of the bio-oil. In particular, the hydrogen yield significantly increased with increasing the current. Several factors should be considered to account for the current effects, as mentioned below. Firstly, the supplied current would enhance the decomposition of the oxygenated organic compounds (C<sub>n</sub>H<sub>m</sub>O<sub>k</sub>) in the bio-oil. Bio-oil, derived from biomass via fast pyrolysis process, generally contains numerous and complex oxygenated organic compounds, which include acids, alcohols, aldehydes, ketones, substituted phenolics and other oxygenates derived from biomass carbohydrates and lignin [10–14]. Hydrogen can be directly produced by the decomposition of these oxygenated organic compounds in the bio-oil [3–5]. In addition, the decomposition can form a series of the intermediates such as H, OH, and CH *etc.*. The intermediates may react with other organic

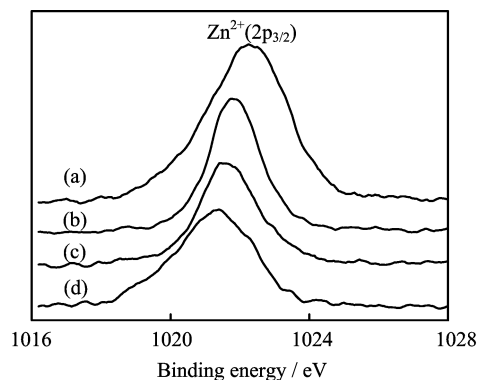


FIG. 8 Zn XPS spectra for (a) fresh CoZnAl catalyst, (b) the used CoZnAl catalyst after the CSR for 5 h (reforming conditions:  $I=0$  A,  $T=600$  °C,  $S/C=7.0$ ,  $GHSV=6200$  h<sup>-1</sup>, and  $P=101$  kPa), (c) the used CoZnAl catalyst after the ECR reforming for 5 h, reforming conditions:  $I=2.0$  A,  $T=600$  °C,  $S/C=7.0$ ,  $GHSV=6200$  h<sup>-1</sup>, and  $P=101$  kPa, and (d) the treated CoZnAl catalyst via a current passing through the catalyst under the argon ambience for 10 h (treatment conditions:  $I=2.2$  A,  $T=600$  °C,  $GHSV=6200$  h<sup>-1</sup>, and  $P(\text{Ar})=101$  kPa), respectively.

compounds and/or water, speeding up the reforming reactions and/or further decomposition. Secondly, the thermal electrons, originating from the electrified wire, promoted the decomposition and reforming of the bio-oil in the ECR process. The presence of the thermal electrons both on the electrified Ni-Cr wire and on the electrified catalyst surface was directly observed by the anionic TOF measurements in our previous work [52–54]. It is well known that when heating an electrified metal or a metal oxide, electrons can boil off its surface, leading to thermal electrons emission from surface [57]. 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.*,  $\text{O}_2+4\text{e}^- \rightarrow 2\text{O}^{2-}$ ), and in the molecular decomposition or ionization processes [58, 59]. Small molecular dissociation of O<sub>2</sub>, H<sub>2</sub>, F<sub>2</sub>, H<sub>2</sub>O and C<sub>6</sub>H<sub>6</sub> via the thermal electrons has also been observed on the Ca-Al-O oxides surface [60, 61]. The promoting effect of the thermal electrons on the molecular decomposition, the reforming, and the catalyst reduction is also supported by our previous work on the ECR reforming of acetic acid and ethanol [53, 54]. Accordingly, the thermal electrons may play an important role in promoting the bio-oil decomposition, its reforming and the catalyst reduction, partly leading to the increase of the hydrogen yield during the ECR process. Thirdly, it was also noticed that the ECR mode (*i.e.*, inner heating) and CSR mode (*i.e.*, outside heating) have different temperature distribution in the catalyst bed. The maximal temperature gradients in ECR were higher than those in CSR. Even though temperature in the center of the catalyst bed is almost close to the average value in the catalyst bed in our investigated range (400–600 °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. Thus, 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 an increase of the overlap hydrogen yield during the ECR process. Further work is still required to clearly understand the reforming mechanism in the ECR process. Work toward this goal is in progress.

#### IV. CONCLUSION

This work reported high efficient production of hydrogen from low-temperature reforming of bio-oil using the electrochemical catalytic reforming approach over the CoZnAl catalyst. The catalyst possesses high activity for the bio-oil reforming reactions under lower operating temperature (400–500 °C), reaching hydrogen yield of 70% and carbon conversion of 85% at 500 °C. The performance of the bio-oil reforming is also significantly promoted by the current through the catalyst. The supplied current through the catalyst bed provided abundant thermal electrons, enhanced the decomposition of the oxygenated organic compounds in the bio-oil and promoted the catalyst reduction. The developed electrochemical catalytic approach and the CoZnAl catalyst would be one of most suitable candidates for the bio-oil reforming because it can efficiently reform the bio-oil to H<sub>2</sub> (63%–66%) and CO<sub>2</sub> (28%–30%) at a lower operating temperature (400–500 °C), as compared with conventional NiO–Al<sub>2</sub>O<sub>3</sub> catalysts (600–850 °C). Present method, potentially, may be a useful route to practically produce H<sub>2</sub> from bio-oil or other hydrocarbons.

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- [1] P. D. Vaidya and A. E. Rodrigues, *Chem. Eng. J.* **117**, 39 (2006).
- [2] A. Haryanto, S. Fernando, N. Murali, and S. Adhikari, *Energy Fuels* **19**, 2098 (2005).
- [3] D. Das and T. N. Veziroglu, *Int. J. Hydrogen Energy* **26**, 13 (2001).
- [4] J. D. Holladay, J. Hu, D. L. King, and Y. Wang, *Catal. Today* **139**, 244 (2009).
- [5] G. W. Huber, J. W. Shabaker, and J. A. Dumesic, *Science* **300**, 2075 (2003).
- [6] E. Chornet and S. Czernik, *Nature* **418**, 928 (2002).
- [7] R. D. Cortright, R. R. Davda, and J. A. Dumesic, *Nature* **418**, 964 (2002).
- [8] J. Corella, J. M. Toledo, and G. Molina, *Ind. Eng. Chem. Res.* **46**, 6831 (2007).
- [9] S. Czernik and A. V. Bridgwater, *Energy Fuels* **18**, 590 (2004).
- [10] X. F. Zhu, J. L. Zheng, Q. X. Guo, and Q. S. Zhu, *J. Environ. Sci.* **18**, 392 (2006).
- [11] X. F. Zhu and R. Venderbosch, *Fuel* **84**, 1007 (2005).
- [12] J. L. Zheng, X. F. Zhu, Q. X. Guo, and Q. S. Zhu, *Waste Management* **26**, 1430 (2006).
- [13] X. F. Zhu, China Pat.00241135.0, (2001).
- [14] X. F. Zhu, China Pat.01263584.7, (2002).
- [15] S. Czernik, R. Evans, and R. French, *Catal. Today* **129**, 265 (2007).
- [16] C. Rioche, S. Kulkarni, F. C. Meunier, J. P. Breen, and R. Burch, *Appl. Catal. B* **61**, 130 (2005).
- [17] D. L. Trimm, *Catal. Today* **37**, 233 (1997).
- [18] A. N. Fatsikostas and X. E. Verykios, *J. Catal.* **225**, 439 (2004).
- [19] M. Nurunnabi, K. Fujimoto, K. Suzuki, B. T. Li, S. Kado, K. Kunimori, and K. Tomishige, *Catal. Commun.* **7**, 73 (2006).
- [20] D. Wang, S. Czernik, D. Montané, M. Mann, and E. Chornet, *Ind. Eng. Chem. Res.* **36**, 1507 (1997).
- [21] L. Garcia, R. French, S. Czernik, and E. Chornet, *Appl. Catal. A* **201**, 225 (2000).
- [22] T. Davidian, N. Guilhaume, E. Iojoiu, H. Provendier, and C. Mirodatos, *Appl. Catal. B* **73**, 116 (2007).
- [23] J. Llorca, P. R. Piscina, J. Dalmon, J. Sales, and N. Homs, *Appl. Catal. B* **43**, 355 (2003).
- [24] A. C. Basagiannis and X. E. Verykios, *Catal. Today* **127**, 256 (2007).
- [25] D. Wang, S. Czernik, and E. Chornet, *Energy Fuels* **12**, 19 (1998).
- [26] P. N. Kechagiopoulos, S. S. Voutetakis, A. A. Lemonidou, and I. A. Vasalos, *Energy Fuels* **20**, 2155 (2006).
- [27] C. M. Kinoshita and S. Q. Turn, *Int. J. Hydrogen Energy* **28**, 1065 (2003).
- [28] V. Fierro, V. Klouz, O. Akdim, and C. Mirodatos, *Catal. Today* **75**, 141 (2002).
- [29] F. Marino, M. Boveri, G. Baronetti, and M. Laborde, *Int. J. Hydrogen Energy* **29**, 67 (2004).
- [30] F. Marino, M. Boveri, G. Baronetti, and M. Laborde, *Int. J. Hydrogen Energy* **26**, 665 (2001).
- [31] A. N. Fatsikostas, D. I. Kondarides, and X. E. Verykios, *Chem. Commun.* 851 (2001).
- [32] M. A. Goula, S. K. Kontou, and P. E. Tsiakaras, *Appl. Catal. B* **49**, 135 (2004).
- [33] J. A. Torres, J. Llorca, A. Casanovas, M. Dominguez, J. Salvado, and D. Montane, *J. Power Sources* **169**, 158 (2007).
- [34] V. A. O'Shea, R. Nafria, and P. R. Piscina, N. Homs, *Int. J. Hydrogen Energy* **33**, 3601 (2008).
- [35] G. Jacobs, R. A. Keogh, and B. H. Davis, *J. Catal.* **245**, 326 (2007).
- [36] A. C. Basagiannis and X. E. Verykios, *Int. J. Hydrogen Energy* **32**, 3343 (2007).
- [37] J. R. Galdamez, L. Garcia, and R. Bilbao, *Energy &*

- Fuels **19**, 1133 (2005).
- [38] K. Takanabe, K. Aika, K. Seshan, and L. Lefferts, *J. Catal.* **227**, 101 (2004).
- [39] K. Takanabe, K. Aika, K. Inazu, T. Baba, K. Seshan, and L. Lefferts, *J. Catal.* **243**, 263 (2006).
- [40] K. Takanabe, K. Aika, K. Seshan, and L. Lefferts, *Chem. Eng. J.* **120**, 133 (2006).
- [41] K. Faungnawakij, R. Kikuchi, T. Fukunaga, and K. Eguchi, *Catal. Today* **138**, 157 (2008).
- [42] F. Haga, T. Nakajima, S. Yamashita, and S. Mishima, *Kinet. Catal. Lett.* **63**, 253 (1998).
- [43] J. Llorca, N. Homs, and P. R. Piscina, *J. Catal.* **227**, 556 (2004).
- [44] M. S. Batista, R. K. S. Santos, E. M. Assaf, J. M. Assaf, and E. A. Ticianelli, *J. Power Sources* **124**, 99 (2003).
- [45] H. Song, L. Z. Zhang, and U. S. Ozkan, *Green Chem.* **9**, 686 (2007).
- [46] M. S. Batista, R. K. S. Santos, E. M. Assaf, J. M. Assaf, and E. A. Ticianelli, *J. Power Sources* **134**, 27 (2004).
- [47] X. F. Zhu, China Pat.00241135.0, (2001).
- [48] X. F. Zhu, J. L. Zheng, Q. X. Guo, and Q. S. Zhu, *J. Environ. Sci.* **18**, 392, (2006).
- [49] Z. X. Wang, Y. Pan, T. Dong, X. F. Zhu, T. Kan, and L. X. Yuan, *Appl. Catal. A Gen.* **320**, 24, (2007).
- [50] T. Dong, Z. X. Wang, L. X. Yuan, Y. Torimoto, M. Sadakata, and Q. X. Li, *Catal. Lett.* **119**, 29 (2007).
- [51] Z. X. Wang, T. Dong, L. X. Yuan, T. Kan, X. F. Zhu, and Y. Torimoto, *Energy Fuels* **21**, 2421, (2007).
- [52] L. X. Yuan, Y. Q. Chen, C. F. Song, T. Q. Ye, Q. X. Guo, Q. S. Zhu, Y. Torimoto, and Q. X. Li, *Chem. Commun.* 5215 (2008).
- [53] L. X. Yuan, T. Q. Ye, F. Y. Gong, Q. X. Guo, Y. Torimoto, M. Yamamoto, and Q. X. Li, *Energy Fuels* **23**, 3101, (2009).
- [54] Y. Q. Chen, L. X. Yuan, T. Q. Ye, S. B. Qiu, X. F. Zhu, Y. Torimoto, M. Sadakata, and Q. X. Li, *Int. J. Hydrogen Energy* **34**, 1760, (2009).
- [55] T. Q. Ye, L. X. Yuan, Y. Q. Chen, and Q. X. Li, *Catal. Lett.* **127**, 323 (2009).
- [56] M. N. Barroso, M. F. Gomez, L. A. Arrúa, and M. C. Abello, *Appl. Catal. A* **304**, 116 (2006).
- [57] G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, New York: Wiley-Interscience, (1994).
- [58] E. V. Tsipis and V. V. Kharton, *J. Sol. Stat. Electrochem.* **12**, 1367 (2008).
- [59] M. B. Ricoult, *Sol. Stat. Sci.* **10**, 670 (2008).
- [60] F. Huang, J. Li, L. Wang, T. Dong, J. Tu, Y. Torimoto, M. Sadakata, and Q. X. Li, *J. Phys. Chem. B* **109**, 12032 (2005).
- [61] J. Li, F. Huang, L. Wang, Z. X. Wang, S. Q. Yu, Y. Torimoto, M. Sadakata, and Q. X. Li, *J. Phys. Chem. B* **109**, 14599 (2005).