Electrochemical catalytic reforming of oxygenated-organic compounds: a highly efficient method for production of hydrogen from bio-oil†

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A novel approach to produce hydrogen from bio-oil was obtained with high carbon conversion (>90%) and hydrogen yield (>90%) at $T < 500$ °C by using the electrochemical catalytic reforming of oxygenated-organic compounds over 18%NiO/Al_2O_3 reforming catalyst; thermal electrons play important promoting roles in the decomposition and reforming of the oxygenated-organic compounds in the bio-oil.

Hydrogen is an important raw material for the chemical industry and it is a potential clean fuel which could have an important role in reducing environmental emissions for the future.[1,2] In particular, its production is a very attractive subject for fuel cell applications,[3,4] which are considered to have the potential to provide a clean energy source for hydrogen-powered vehicles as an alternative to gasoline or diesel engines.[1,2] Currently, commercially used hydrogen is mainly produced on a large scale by steam reforming of natural gas.[5] However, the production of hydrogen from fossil fuels will increase the emission amounts of carbon dioxide and local pollution. By contrast, production of hydrogen from lignocellulosic biomass, an environmentally friendly and rich feedstock, would open a new prospect for the utilization of the renewable biomass sources.[6–8]

The route of the steam reforming of bio-oil involves fast pyrolysis of biomass to generate bio-oil and reforming of it to produce a gaseous rich-hydrogen mixture. Bio-oil also represents another potential source of renewable chemicals.[9] Production of hydrogen from bio-oil reforming is probably one of the most promising options because it can achieve high hydrogen yield and high content of hydrogen. So far, it has been explored for the steam reforming of bio-oil *via* various catalysts such as Ni-based catalyst[10] and noble metal catalysts.[11] However, two problems, exorbitant reforming temperature and catalyst deactivation, remain serious challenges in the production of hydrogen from bio-oil.[10–12] Much of our attention has been paid to the production of bio-oil, hydrogen and liquid bio-fuels.[12–14] Here, we show a novel and efficient low-temperature reforming approach for production of hydrogen from bio-oil by using the electrochemical catalytic reforming (ECR) of organic compounds over a conventional Ni-based reforming catalyst. We also demonstrate that the thermal electrons on the catalyst surface play important roles in the reforming reactions of the organic compounds.

The 18%NiO/Al_2O_3 catalyst was prepared by the impregnation of Al_2O_3 with $Ni(NO_3)_2$ aqueous solution, then the slurry was dried at 110 °C for 24 h, and finally calcined at 500 °C for 2 h. The nickel loading in the resulting catalyst was about 18 wt% and its BET surface area was 115.1 $m^2 g^{-1}$. The bio-oil, produced by fast pyrolysis of sawdust, is represented by the chemical formula $CH_{2.03}O_{0.67}\cdot 0.89H_2O$ (see ESI†). Reforming of bio-oil was performed in the quartz fixed-bed reactor under 1 atm. The reaction system, operating procedures and analysis of the products were described in detail in ESI.† Here, two bio-oil reforming models, *i.e.*, the common steam reforming (CSR) and electrochemical catalytic reforming (ECR), were compared. For ECR, the catalyst was uniformly embedded around an electrified annular Ni–Cr wire, used for providing thermal electrons onto the catalyst and heating the catalyst bed. In case of CSR, ac current was shut off and the catalyst bed was heated by an outside furnace (Fig. I in ESI†). The temperature distribution in the catalyst bed was tested before running the reforming experiments.

The reforming performance of the bio-oil using the CSR method, generally, was mainly controlled by temperature (T) and S/C (the ratio of steam to carbon fed) for a given catalyst. In this work, it was observed interestingly that the behavior of the reforming was very sensitive to the current (I) through the catalyst (*i.e.*, ECR). To investigate the features of ECR, we performed the bio-oil reforming under different currents, while other experimental conditions were maintained at fixed parameters. Fig. 1(a) shows the dependence of the carbon conversion on the current (I) at different fixed temperatures. In the case of $I = 0$ (*i.e.*, CSR), the carbon conversion was only 14.7% at 400 °C, and increased to 65.4% at 600 °C. However, on the current flowing through the 18%NiO/Al_2O_3 catalyst (*i.e.*, ECR), the carbon conversion was remarkably enhanced, particularly at lower temperature. The carbon conversion significantly increased from 14.7 to 72.7% at 400 °C with increasing the current from 0 to 3.8 A, and reached 96.5% at 500 °C and 3.8 A. The yield of hydrogen also remarkably increased from 35.6 to 95.8% with increasing the current from 0 to 3.8 A at 500 °C (Fig. 1(b)).

Fig. 2 depicts the influence of the current on the composition of the gaseous products. Hydrogen is the major product

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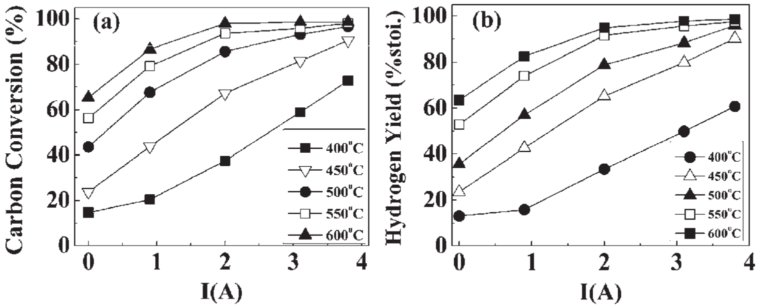

Fig. 1 (a) Effect of the current on the carbon conversion, and (b) influence of the current on the hydrogen yield, measured as a function of current through the 18%NiO/Al_2O_3 catalyst at different fixed temperatures, Other reforming conditions: $S/C = 5.8$, GHSV = 6048 h^{-1}, and $P = 1$ atm.

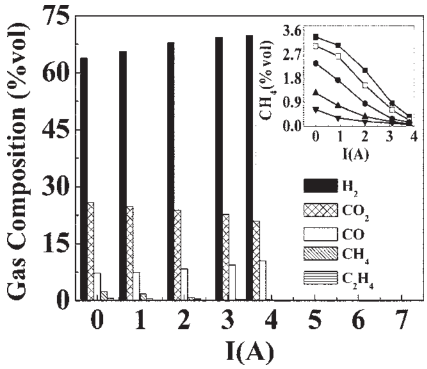

Fig. 2 Influence of the current on the gaseous product compositions of H_2, CO_2, CO, CH_4 and C_2H_4 over the 18%NiO/Al_2O_3 catalyst. Reforming conditions: $T = 500$ °C, $S/C = 5.8$, GHSV = 6048 h^{-1}, and $P = 1$ atm. Inset: the content of CH_4 *vs.* the current (■: 400 °C, □: 450 °C, ●: 500 °C, ▲: 550 °C, ▼: 600 °C).

together with small amounts of CO_2 and CO. A trace amount of CH_4 and/or C_2H_4 was also observed in the effluent carbonaceous compounds. It was found that the concentrations of H_2 and CO increased with increasing the current, accompanied by a decrease of CO_2, CH_4 or C_2H_4. In particular, the CH_4 content in the un-reformed by-products was near zero at higher current. Based on the estimation of the mass-balance for the C, H, O elements, most of the carbon and oxygen in the bio-oil was converted into CO_2 and CO (Table VI in ESI†).

The influences of current on the microcosmic properties of the catalyst were also investigated (Table IV in ESI†). In comparison with the fresh catalyst, the BET surface areas and pore volume from the used ones after CSR or ECR slightly decreased, accompanied by an increase of the pore diameter and the size of the crystallites. After a current passed through the catalyst under argon, a slight decrease of the BET surface area together with an increase of the crystallite size was also observed. Generally, the decrease of the BET surface area or the increase of the crystallite size will lead to the decrease of the catalyst activity. However, it was observed that the current applied in ECR obviously promoted the production of hydrogen from the bio-oil. Based on the stability test of the catalyst, no obvious change of the hydrogen yield was observed for the initial 5 h in ECR. The above results indicate that the alterations of the catalyst properties induced by the current over the initial 5 h would have a minor influence on the production of hydrogen from ECR of the bio-oil.

The NiO reduction in CSR and ECR were investigated by XPS and XRD measurements (ESI†). Ni is nearly in the +2 "formal" oxidation state in the freshly prepared catalyst. After the CSR for 5 h, part of Ni^{2+} both on the catalyst surface and inside the catalyst was reduced to metallic Ni^0 through the reaction of $NiO + H_2 \rightarrow Ni^0 + H_2O$, where H_2 was produced by the bio-oil reforming. The reduction level of the catalyst surface *via* the XPS measurements for ECR, described by the ratio of $r = [Ni^0]_s/([Ni^0]_s + [Ni]^{2+}{}_s)$, was about 50.8%, which was obviously higher than the value of 28.7% from CSR. The reduction level inside the catalyst *via* the XRD measurements for ECR (described by the ratio of $r = [Ni^0]_b/([Ni^0]_b + [Ni^{2+}]_b)$) was about 52.1%, which was also higher than the value from CSR (29.7%, Table IV in ESI†). The above results indicated that an additional number of Ni^{2+} was reduced to the metallic Ni^0 after ECR. The additional reduction was attributed to the reaction of the ionic state Ni^{2+} with the thermal electrons (*i.e.*, $Ni^{2+} + 2e^- \rightarrow Ni^0$). This explanation was supported by two facts: (1) the desorption of the thermal electrons from the electrified catalyst was directly observed (Fig. 3) and (2) the reduction behavior was also observed when a current was passed through the catalyst under argon (Fig. II(d) in ESI†).

The differences of the initial reforming performances between the $NiO–Al_2O_3$ and $Ni–Al_2O_3$ catalysts were compared both for ECR and CSR (Fig. III in ESI†). Both the $NiO–Al_2O_3$ and $Ni–Al_2O_3$ catalysts show catalytic activity for the bio-oil

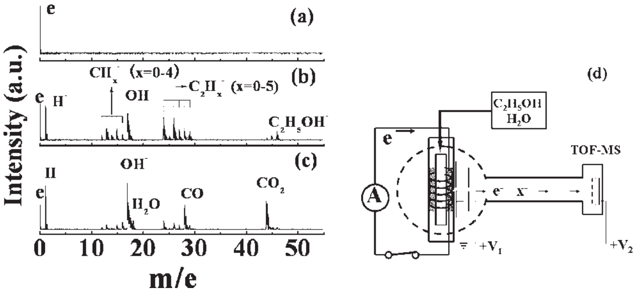

Fig. 3 Typical TOF spectra measured under a variety of experimental conditions. (a) Current passed through the 18%NiO/Al_2O_3 catalyst under argon ($I = 3.0$ A, $T = 580$ °C, $P(Ar) = 2.9 \times 10^{-1}$ Pa); (b) with a mixture of C_2H_5OH–Ar fed onto the electrified 18%Ni/Al_2O_3 catalyst ($I = 2.9$ A, $T = 580$ °C, $P(C_2H_5OH) = 0.5 \times 10^{-1}$ Pa, $P(Ar) = 2.3 \times 10^{-1}$ Pa); (c) with a mixture of H_2O–C_2H_5OH–Ar fed onto the electrified catalyst ($I = 3.0$ A, $T = 580$ °C, $P(C_2H_5OH) = 0.4 \times 10^{-1}$ Pa, $P(H_2O) = 1.4 \times 10^{-1}$ Pa, $P(Ar) = 1.0 \times 10^{-1}$ Pa). (d) A schematic for the TOF experimental set-up.

reforming. The reforming activity over the Ni–Al_2O_3 catalyst is somewhat higher than that over the NiO–Al_2O_3 catalyst in our investigated region. In particular, the prominent influence of the current on the yield of hydrogen was also observed for the Ni–Al_2O_3 catalysts. This means that the significant promoting effects of the current on the production of hydrogen from the bio-oil, observed in the ECR process *via* the NiO–Al_2O_3 catalyst, could not be mainly attributed to the reduction of NiO into Ni. Most probably, the thermal electrons would play an important role in promoting the decomposition and reforming of the oxygenated organic compounds ($C_nH_mO_k$) in the bio-oil as described below.

The influence of current on the decomposition of the oxygenated organic compounds ($C_nH_mO_k$) in the bio-oil as well as a model oxygenated organic compound (acetic acid) was investigated by homogeneous experiments over a quartz sand bed under conditions with and without current (Table V in ESI†). Both the carbon conversion and hydrogen yield remarkably increased with increasing the current, indicating that the decomposition of the oxygenated organic compounds was promoted by the current. The promoting effects of current on the decomposition would be explained by the decomposition of the molecule *via* thermal electrons.

When an ac electronic current passes through a metal wire the electrons will flow through the electrified wire and some will leave the metal surface and form thermal electrons in the gas phase (*i.e.*, thermal electron emission).[15–17] The thermal electrons may promote the dissociation of the oxygenated organic molecules in the bio-oil, and the reforming reactions. To confirm the above conjecture, we carried out the following low-pressure (10^{-1} Pa) ECR reactions using ethanol as a model of the oxygenated organic compounds for simplifying the reaction system. Fig. 3(a) shows typical time-of-flight (TOF) mass spectra when current was passed through the 18%NiO/Al_2O_3 catalyst under argon. Only one peak at m/z = 0 was observed, corresponding to the thermal electrons desorbed from the electrified catalyst surface. When the mixture of C_2H_5OH/Ar was fed onto the electrified catalyst, a series of new peaks of H^-, OH^-, CH_x^- (x = 0–4), $C_2H_x^-$ (x = 0–5), $C_2H_5OH^-$ appeared (Fig. 3(b)). The hydrocarbon fragments would form *via* the dissociation of ethanol caused by the thermal electrons on the surface (*i.e.*, $e^-(s) + C_2H_5OH(s) \rightarrow C_xH_y^-(s) + \cdots$, where s represents the surface). As the mixture of $H_2O/C_2H_5OH/Ar$ was injected onto the electrified catalyst, the peak of CO_2^- was observed (Fig. 3(c)), indicating that the reforming reaction of ethanol (*i.e.*, $C_2H_5OH(s) + H_2O(s) \rightarrow CO_2(s) + H_2(s)$) occurred. The above results further confirmed that the thermal electrons play an important role in promoting the decomposition and reforming of the oxygenated organic compounds.

In summary, we present a new and effective method for production of hydrogen *via* the electrochemical catalytic reforming of bio-oil over 18%NiO/Al_2O_3 reforming catalyst, giving good reforming performance including high hydrogen yield (>90%) and high carbon conversion (>90%) even at low temperature. The thermal electrons in ECR significantly promoted the dissociation and the reforming reactions of the oxygenated organic compounds in the bio-oil. The energy efficiency in ECR was higher than that in the CSR process (ESI†). The present approach would be a promising option for production of hydrogen from bio-oil with higher energy efficiency and lower cost.

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