

LETTER

Hydrogen Production by Catalytic Steam Reforming of Bio-oil, Naphtha and CH₄ over C12A7-Mg Catalyst

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(Dated: Received on April 29, 2006; Accepted on May 19, 2006)

Hydrogen production by catalytic steam reforming of the bio-oil, naphtha, and CH₄ was investigated over a novel metal-doped catalyst of (Ca₂₄Al₂₈O₆₄)⁴⁺·4O⁻/Mg (C12A7-Mg). The catalytic steam reforming was investigated from 250 to 850 °C in the fixed-bed continuous flow reactor. For the reforming of bio-oil, the yield of hydrogen of 80% was obtained at 750 °C, and the maximum carbon conversion is nearly close to 95% under the optimum steam reforming condition. For the reforming of naphtha and CH₄, the hydrogen yield and carbon conversion are lower than that of bio-oil at the same temperature. The characteristics of catalyst were also investigated by XPS. The catalyst deactivation was mainly caused by the deposition of carbon in the catalytic steam reforming process.

Key words: C12A7-Mg, Bio-oil, Naphtha, CH₄, Catalytic steam reforming, Hydrogen

Hydrogen is an important raw material for the chemical industry and is a clean fuel that can be used in fuel cells to provide electricity. Currently, hydrogen is mainly produced by steam reforming of methane in industry [1]. Steam reforming of naphtha is another important process [2]. However, the hydrogen production from fossil fuels will increase the emission amount of carbon dioxide and result in the greenhouse effect. Recently, a renewable biomass as a feedstock for hydrogen production has attracted much attention, particularly, on converting fast pyrolysis bio-oil into hydrogen by Ni-based catalysts [3-6]. In our studies, we investigate the main process for hydrogen production by the steam reforming of bio-oil, naphtha and CH₄ over a novel C12A7-Mg catalyst.

The bio-oil used for the catalytic steam reforming was produced by fast pyrolysis of biomass in our biomass clean energy laboratory [7,8]. The bio-oil was a complex mixture including carboxylic acids, aldehydes, alcohols, lignin-derived aromatic phenolics, etc. The bio-oil comprised (wt%) 30.2% carbon, 8.68% hydrogen, 60.8% oxygen, and with a water content of 25.2%, which can be presented as a chemical formula of C_nH_mO_k (CH_{2.33}O_{0.95}·0.56H₂O). About 60% materials of the bio-oil can be volatile (including H₂O), the most abundant of which (at the level of several percent) are acetic and formic acids, acetol, and so on.

The C12A7-O⁻ sample was prepared by a solid-state reaction at 1350 °C for 16 h. The more detailed preparation procedures have been described elsewhere [9,10]. To prepare the magnesium-doped C12A7 cata-

lyst, the C12A7-O⁻ pellet was powdered and mechanically mixed with 30wt% MgO. Finally, these mixtures were calcined at 900 °C for 4 h under flowing dry oxygen atmosphere.

The experiments of the catalytic steam reforming of the bio-oil, naphtha and CH₄ were carried out in a continuous flowing system using a fixed bed micro-reactor which filled with about 200 mg catalyst powder (60-80 mesh size) under atmospheric pressure. When the reaction temperature was reached, we first convert the bio-oil (or naphtha) into vapor and then feed the vapor into the reactor with steam at the space velocity of about 10000 h⁻¹ (G_{C1}HSV defined as C₁ equivalent volume of feed per hour per unit volume of catalyst). The product gas was analyzed by two on-line gas chromatographs (GC) with a thermal conductivity detector (TCD). H₂, CO and CH₄ were detected by GC1 (Molecular Sieve 5 Å). CO₂ and C₂ hydrocarbons (e.g. C₂H₄ and C₂H₆ etc.) were detected by GC2 (GDX-502). The characteristic of catalyst was also investigated by XPS and the C1s peak at 284.6 eV was used as a standard for the XPS measurements.

The steam reforming of the bio-oil, naphtha and CH₄ can be simplified as the catalytic steam reforming of the oxygenated organic compound (C_nH_mO_k) by the following reaction:

$$C_nH_mO_k + (n - k)H_2O = nCO + (n + m/2 - k)H_2 \quad (1)$$

The above reaction is followed by the water-gas shift reaction:

$$nCO + nH_2O = nCO_2 + nH_2 \quad (2)$$

Therefore, the overall process can be represented as follows:

$$C_nH_mO_k + (2n - k)H_2O = nCO_2 + (2n + m/2 - k)H_2 \quad (3)$$

The process performance was measured by hydrogen yield calculated as the percentage of the stoichiometric

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potential, assuming complete conversion of carbon to CO₂ according to the reaction (3). Thus the potential yield of hydrogen gas from an oxygenated feedstock is $(2 + m/2n - k/n)$ moles of H₂ per mole of carbon in the feed [11]. The carbon conversion was calculated by the total carbon-moles in the product gases divided by the carbon-moles fed.

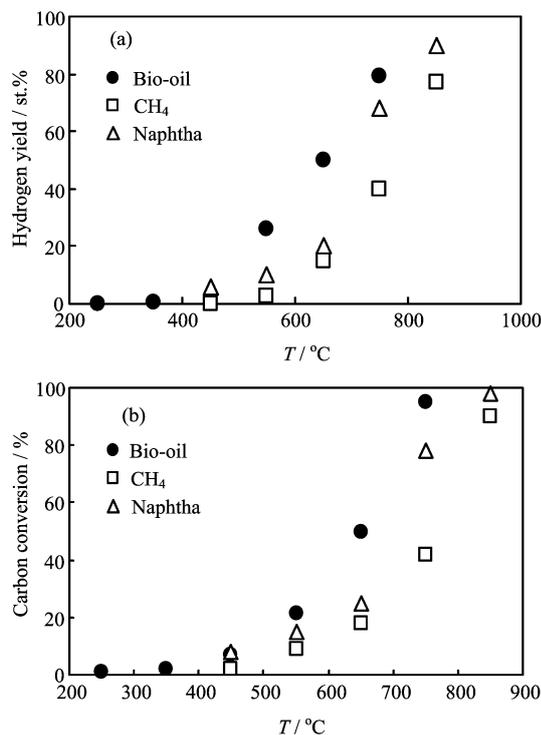


FIG. 1 The hydrogen yield and carbon conversion for the catalytic steam reforming of the bio-oil, naphtha and CH₄ were measured as a function of temperature at $S/C=4.0$ and $GHSV=10000 \text{ h}^{-1}$ over the C12A7-Mg catalyst.

Among the important parameters for steam reforming are temperature (T), molar steam-to-carbon ratio (S/C) and methane-equivalent gas hourly space velocity ($G_{C1}HSV$), temperature is found to have the most significant effect on catalytic steam reforming reactions. The hydrogen yield and the carbon conversion have been measured as a function of the reforming temperature. Figure 1(a) shows the effect of temperature on the hydrogen yield for a typical catalytic steam reforming condition of bio-oil, naphtha and CH₄ over the C12A7-Mg catalyst (The catalyst: 200 mg, $S/C=4.0$, $GHSV=10000 \text{ h}^{-1}$). For bio-oil, the hydrogen yield is lower than 5% with the temperature below 450 °C. The hydrogen yield significantly increases with increasing temperature in the temperature range of 550-750 °C, and gives a maximum value of about 80% within our investigated region. On the other hand, the carbon conversion also increases with increasing temperature, as shown in Fig.1(b). Total carbon conversion is near 95%

at 750 °C, which is much higher than Ni-based catalysts at the same temperature [6]. For the reforming of naphtha and CH₄, the hydrogen yield and carbon conversion are lower than that of bio-oil at the same temperature. Both of them produce a little H₂ below 450 °C. The hydrogen yield and carbon conversion also significantly increase when temperature increases. For the reforming of naphtha, the hydrogen yield reaches 90% at 850 °C with total carbon conversion of 98%. For the reforming of CH₄, the hydrogen yield reaches a value of about 77% at 850 °C with total carbon conversion of 90%. The bio-oil comprised mainly unstable oxygenated organic compounds, while naphtha and CH₄ were stable hydrocarbon. So it is easier for reforming of bio-oil than naphtha and CH₄ at the same reforming conditions. All of the above results indicate that C12A7-Mg is a good catalyst for steam reforming of hydrocarbon and oxygenated organic compounds.

We have also examined the stability of the C12A7-Mg catalyst for the reforming of the bio-oil. It was found that the lifetime of the C12A7-Mg catalyst is about 210 min at 750 °C (the hydrogen yield gradually decreases from about 80% to 50% during the initial 3.5 h), which is four times as long as Ni-based catalysts [6].

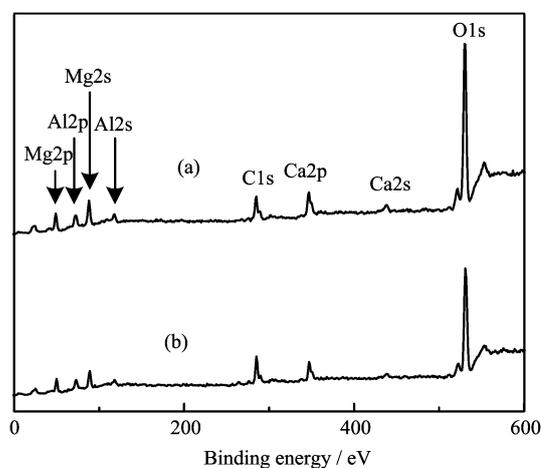


FIG. 2 XPS spectra for C12A7-Mg samples (a) before the reforming (fresh sample) and (b) after the reforming of the bio-oil at 750 °C and $S/C=4.0$ for 4 h. The peak of C1s arose from C1s A (carbon deposition) and C1s B (CO₃²⁻).

Figure 2 shows the XPS spectrum for the C12A7-Mg sample before and after the reforming of bio-oil. By comparing the peak positions with the data in the NIST Databases, the peaks at 49.67, 72.45, 346.85 and 530.65 eV, have been assigned to Mg2p, Al2p, Ca2p, O1s, respectively. As shown in the XPS spectra, compared with the fresh sample, no new peaks were found for the reacted sample. However, the spectral intensities of Mg2p, Mg2s and C1s have been obvious changed after the catalytic steam reforming of the bio-oil. As

can be seen from Table I, the content of carbon on the surface of the catalyst increases, which is caused by the deposition of carbon during the steam reforming process. The decrease of the Mg content on the surface of the catalyst has been also confirmed. In our previous work [12], MgO has been confirmed as active composition in C12A7-Mg catalyst. The above results indicate that the catalyst deactivation was mainly caused by the deposition of carbon which poisoned the active surface and the content decrease of the active compositions (MgO) on the catalyst surface in the reforming process of bio-oil. The steam reforming of CH₄ and naphtha has the similar XPS results to the bio-oil (not shown here). It can also be found from the XPS summary that there is a little C on the catalyst surface: 11.5mol% in the reforming of CH₄, 14.7mol% in the reforming of naphtha, and 19.7mol% in the reforming of bio-oil. It indicates that the process of steam reforming of bio-oil may cause more carbon deposition than reforming CH₄ and naphtha, which is probably caused by thermal decomposition reaction of the unstable compounds in the bio-oil.

TABLE I The changes of elemental composition on the surface of C12A7-Mg samples after the reforming of the bio-oil at 750 °C and *S/C*=4.0 for 4 h (XPS summary).

Elemental composition /(mol%)	Fresh sample (a)	After the reforming of the bio-oil (b)
Mg2p	16.9	14.2
C1s A(carbon deposition)	12.2	19.7
C1s B(CO ₃ ²⁻)	4.5	5.5

In conclusion, the C12A7-Mg catalyst shows a good performance for hydrogen generation from the catalytic steam reforming of the bio-oil, naphtha and CH₄ at relatively low temperature and with longer lifetime compared to Ni-based catalyst. The maximum hydrogen yield of 80% was obtained at

750 °C for bio-oil. For the reforming of naphtha and CH₄, the hydrogen yield and carbon conversion are lower than that of bio-oil at the same temperature. The catalyst deactivation was mainly caused by the deposition of carbon in the catalytic steam reforming process. Further work to make a clearer description for the steam forming process is in progress.

ACKNOWLEDGMENT

This work was supported by BRP program 2002 and Innovation Program 2002 of Chinese Academy of Sciences.

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