Steam Reforming of Acetic Acid to Hydrogen over Fe–Co Catalyst

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The steam reforming of acetic acid to hydrogen was investigated over Fe–Co catalyst. The influence of temperature, liquid hourly space velocity, and molar ratio of steam-to-carbon were studied in detail. At 400 °C, acetic acid was converted completely. The selectivities of H_2 and CO_2 reached maximum values 95.3 and 92.9%, respectively.

Hydrogen is recognized as a clean fuel and energy carrier in the future economy. Most hydrogen now is produced from fossil such as natural gas, naphtha, and coal.[1] Growing environmental concerns, global warming and fast depletion of fossil fuel reserves resulted in extensive research in renewable energy technology. Flash pyrolysis of biomass to bio-oil and its steam reforming is one of the choices.[2] Acetic acid is one of the major components in bio-oil.[3,4] Therefore, study of steam reforming of acetic acid can provide valuable method for hydrogen production from biomass. Acetic acid is renewable and can be easily obtained from biomass by fermentation. In addition, acetic acid, unlike methanol and ethanol, is nonflammable, so it is a safe hydrogen carrier. Up to now, only very limited reports[4–10] have been published on hydrogen production from acetic acid. Usually, the temperature conducted in the reaction was higher than 600 °C.

In this paper, a new catalyst for acetic acid reforming was reported. The conversion and selectivity for hydrogen reached about 100 and 90% at 400 °C respectively. To our knowledge, such low reaction temperature has not been reported.

Fe–Co catalyst was prepared by coprecipitation method. The catalyst precursors were prepared by adding aqueous mixture solution of metal salts, $Fe(NO_3)_2$, $Co(NO_3)_2$ (molar ratio 1:0.5), to a vigorously stirred solution of Na_2CO_3 at room temperature. The resulted precipitate was filtered, washed with distilled water until pH was 7, and then dried in air at 110 °C overnight. Then, the coprecipitated catalyst precursor was calcined in air at 500 °C for 3 h and crashed to 0.20–0.56 mm.

Catalytic activities were tested in a fixed bed continuous flow quartz reactor at normal pressure from 250 to 550 °C. Typically, 1 mL of catalyst was used in each run and diluted with an equal amount of quartz. The calcined catalyst was reduced in situ by 50% H_2 in N_2 stream (flow rate 60 mL/min) at 400 °C for 3 h prior to use. The acetic acid solution was pumped with a syring into the reactor. Nitrogen was used as carrier gas and internal standard for gas analysis. The gas-phase effluents were analyzed on two on-line chromatographs equipped with thermal-conductivity detectors (TCD). H_2 selectivity was defined as (moles of H_2 production)/(moles of acetic acid consumed × 4) and others were similar to H_2. The X-ray diffraction spectra (XRD) measurements were performed on a Philips X pert MPD instrument using Cu Kα radiation in the scanning angle range of 10–90° at a scanning rate of 4°/min at 40 mA and 50 kV.

Figure 1 shows the effects of reaction temperature on the steam-reforming reaction over Fe–Co catalyst. It can be found that reaction temperature markedly affected acetic acid conversion and H_2 and CO_2 selectivities in the temperature range from 300 to 350 °C. At 300 °C, the conversion of acetic acid was just 10.3%, but the conversion reached 93.7% when the temperature increased to 350 °C. At the same time, a slightly decreased CO selectivity was found, whereas the selectivity of H_2 and CO_2 increased. When the temperature increased to 400 °C, acetic acid was converted completely, and the selectivities of H_2 and CO_2 reached maximum values 95.3 and 92.9%, respectively. When the temperature increased continuously, the selectivity of CH_4 increased, as a result, the selectivities of H_2 and CO_2 slightly decreased. There were trace amount of acetaldehyde and ethylene detected from 300 to 450 °C, but they were too few to be quantified easily, so we did not express them in this figure and the tables below.

It can be found from Table 1 that LHSV affected the conversion of acetic acid significantly. When the LHSV increased from 3.3 to 9.9 h^{-1}, the conversion of acetic acid decreased from 100 to 70.9%. LHSV also affected the selectivities of the products, especially the CO selectivity, which became higher with the increase of LHSV. As a result, the selectivities of H_2 and CO_2 became lower at higher LHSV.[4,6] From the Table 1, we also knew that it was unfavorable for CH_4 generation at higher LHSV.

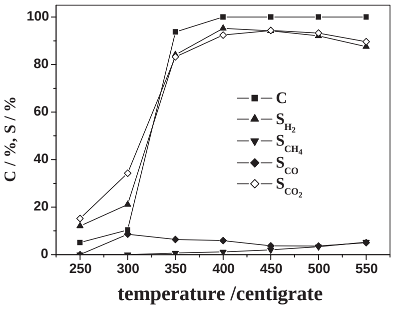

Figure 1. Effects of temperature on the conversion of acetic acid and selectivities of gaseous products. Experimental conditions: S/C mol ratio 7.5:1; LHSV 5.1 h^{-1}; $P = 1$ atm.

Table 1. Effects of liquid hourly space velocity (LHSV) on the conversion of acetic acid and selectivities of gaseous products

LHSV/h^{-1}	C/%	S_{H2}/%	S_{CH4}/%	S_{CO}/%	S_{CO2}/%
3.3	100	97.5	1.5	0	98.4
5.1	100	94.8	1.4	5.8	92.6
7.8	81.1	92.8	0.98	10.3	88.6
9.9	70.9	89.5	0.77	16.9	82.2

Experimental conditions: $t = 400$ °C; S/C mol ratio 7.5:1; $P = 1$ atm.

Table 2. Effects of S/C on the conversion of acetic acid and selectivities of gaseous products

S/C	C/%	S_{H2}/%	S_{CH4}/%	S_{CO}/%	S_{CO2}/%
7.5:1	100	94.8	1.4	5.8	92.6
5:1	73.9	91.1	0.98	13.8	85.1
2.5:1	52.1	87.9	0.93	18.9	80.1

Experimental conditions: $t = 400\,°C$; LHSV $5.1\,h^{-1}$; $P = 1$ atm.

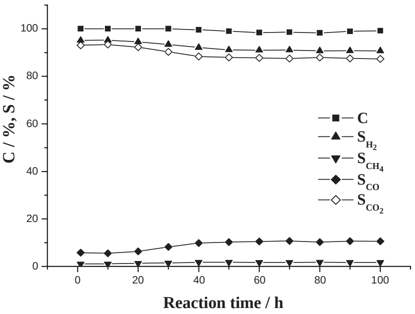

Figure 2. Stability test for acetic acid steam reforming. Experimental conditions: $t = 400\,°C$; S/C mol ratio 7.5:1; LHSV $5.1\,h^{-1}$; $P = 1$ atm.

We also studied the effects of steam-to-carbon molar ratio (S/C) on the reaction. It can be seen from Table 2 that S/C had remarkable effects on the conversion of acetic acid and selectivities of gaseous products. The conversion of acetic acid dropped from 100 to 52.1% when S/C decreased from 7.5:1 to 2.5:1, but the selectivity of CO increased markedly with the decrease of S/C, conversely, the selectivities of H_2 and CO_2 decreased now. Marquevich et al. reported that low S/C resulted in low rate of the steam-reforming reaction due to low partial pressure of steam.[7] In another literature, he pointed out that the organic and steam compete in metal site. As a result, influence the conversion and selectivity.[9]

The stability of the catalyst with time-on-stream was examined at 400 °C for 100 h. It can be seen from the Figure 2 that Fe–Co catalyst maintained its activity and selectivities for the entire 100 h under the experimental conditions. The conversion of acetic acid was about 100% and selectivities of H_2 and CO_2 were around 90% throughout the run time. The selectivity of CO slightly increased during first 40 h while the selectivity of CH_4 kept very low value. No coke was found after the long-term run.[11–13]

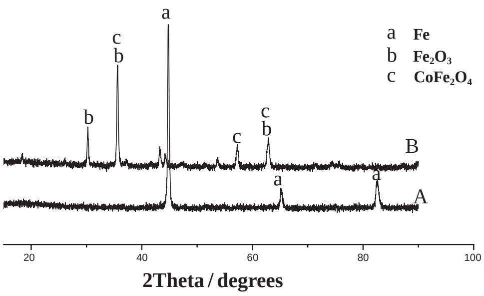

Figure 3. XRD patterns of fresh and used Fe–Co catalysts; A: the fresh catalyst; B: the used catalyst.

X-ray diffraction patters for fresh and used Fe–Co catalysts were presented in Figure 3. It can be seen that the fresh and used catalyst exhibited very different diffraction patterns. For the fresh catalyst, only three peaks attributable to Fe phase were observed at 44.8, 65.2, and 83.6°, which indicated that Co species was highly dispersed or amorphous. For the used catalyst, the diffraction patterns became complicated, which meant that there were reconstruction of the sample happened during the reaction, the Fe phase disappeared, while Fe_2O_3 phase appeared instead. Another new phase found was $CoFe_2O_4$, which indicated that the Fe and Co species might be oxidized during the reaction and formed $CoFe_2O_4$ species which might strengthen the interaction between the Fe and Co species, so we thought $CoFe_2O_4$ species might be responsible for the high activity of Fe–Co catalyst.

To sum up, the present results clarified that a novel Fe–Co catalyst could produce hydrogen via acetic acid steam reforming in low and middle temperature range from 350 to 550 °C effectively. It possessed high activity, selectivity, and good stability.

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