

Investigation of steam reforming of acetic acid to hydrogen over Ni–Co metal catalyst

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Abstract

Catalytic generation of hydrogen by steam reforming of acetic acid over a series of Ni–Co catalysts have been studied. The catalyst with the molar ratio of 0.25:1 between Ni and Co was superior to other catalysts. The effects of reaction temperature, liquid hourly space velocity (LHSV) and molar ratios of steam-to-carbon (S/C) were studied in detail over this catalyst. At $T = 673$ K, $LHSV = 5.1 \text{ h}^{-1}$, $S/C = 7.5:1$, the catalyst exhibited the best performances. Acetic acid was converted completely to hydrogen, while H_2 selectivity reached up to 96.3% and CO_2 selectivity up to 98.1% was obtained, respectively. Ni–Co catalyst showed rather stable performances for the 70 h time-on-stream without any deactivation.

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Keywords: Acetic acid; Hydrogen; Steam reforming; Ni–Co catalyst

1. Introduction

Hydrogen is recognized as a clean fuel and energy carrier in the future economy. Most hydrogen now is produced from fossil fuels such as natural gas, naphtha, and coal [1]. Due to environmental pollution and the high dependence on fossil fuels, the world-wide interest in the energy area now is strongly focused on the production of hydrogen from alternative fuels. Among the several routes, the production of hydrogen from biomass is regarded as one of the main renewable technologies, for it can achieve the zero emissions of carbon dioxide for the carbon cycle in the production process and make us less dependent on fossil fuels for power and transports. Therefore, some methods of producing hydrogen from biomass have been investigated: for example, gasification [2] or flash pyrolysis of biomass to bio-oil and its steam reforming [3–6]. The latter method has attracted considerable interest, for bio-oil as a renewable feedstock was easily to be handled and transported. Bio-oil was a complex

mixture of oxygenate compounds and acetic acid was one of the major components [7,8], therefore, study of steam reforming of acetic acid can provide valuable methods and data for hydrogen production from bio-oil. On the other hand, acetic acid itself is renewable and can be easily obtained from biomass by fermentation. In addition, acetic acid, unlike methanol and ethanol, is nonflammable, hence, it is a safe hydrogen carrier. Acetic acid also can be easily converted to hydrogen with high selectivity at low temperature over effective catalysts such as Ni–Co, so it may be one of the suitable fuels for the proton exchange membrane fuel cells (PEMFC). Up to now, very limited reports [5,6,8–11] in producing hydrogen from acetic acid have been published, and only a few catalysts have been investigated, for example, ICI 46-1 [5,6], UC G-90C [5,6,9], Ni–Al [8], Pt/ZrO₂ [10], Pt, Rh and Pd based catalysts [11] and so on. Moreover, the temperature conducted in the reactions over these catalysts was usually higher than 873 K.

In this paper, a novel catalyst, which was bimetallic and unsupported, was reported for steam reforming of acetic acid. In the temperature range from 623 to 673 K, the catalyst exhibited very good activity and selectivity to hydrogen, both conversion of acetic acid and selectivity to hydrogen exceeded 90%. To our knowledge, such results have not been reported at such low reaction temperature.

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2. Experimental

2.1. Catalysts preparation

A series of Ni–Co catalysts with different Ni and Co ratios were prepared by co-precipitation method. The catalysts precursors were prepared by adding aqueous mixture solution of metal salts, $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, which was depended on the indicated catalyst component, to a vigorously stirred solution of Na_2CO_3 at room temperature. The resulted precipitate was filtered and washed with distilled water until pH was 7, then dried in air at 383 K overnight. Finally, the co-precipitated catalyst precursor was calcined in air at 773 K for 3 h and crashed to 0.20–0.56 mm for testing.

2.2. Catalytic activity measurements

Catalytic performances tests were carried out in a fixed bed continuous flow quartz reactor at normal pressure and temperature from 523 to 823 K. Typically, 1 mL of the catalyst was used in each run and diluted with 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 673 K for 3 h prior to use. Acetic acid solution was pumped with a syringe into the reactor. Nitrogen was used as a 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). Hydrocarbons as well as oxygenated products were separated and analyzed by means of a flame ionization detector (FID). The detection limit for the products was 1×10^{-2} vol.% at the given conditions. At the end of the catalytic tests, the catalyst was cooled under N_2 stream and stored for characterizations in N_2 atmosphere. Steam reforming activity was defined in terms of conversions of acetic acid and selectivities to the products. Conversions of acetic acid were denoted as C , selectivities to the products (hydrogen, carbon dioxide, methane, carbon monoxide and so on) were denoted as S_{product} , which were calculated according to the corresponding equations: $S_{\text{H}_2} (\%) = 100 \times (\text{moles of H}_2 \text{ production}) / (\text{moles of acetic acid consumed} \times 4)$; the calculated method of selectivities to other products were similar to that of H_2 .

2.3. Catalyst characterizations

The X-ray diffraction spectra (XRD) measurements were performed on a Philips Xpert MPD instrument using $\text{Cu K}\alpha$ radiation in the scanning angle range of $10\text{--}90^\circ$ at a scanning rate of $4^\circ/\text{min}$ at 40 mA and 50 kV.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out at room temperature on a VG ESCALAB 210 spectrometer with $\text{Mg K}\alpha$ radiation ($h\nu = 1253.6 \text{ eV}$). If necessary, the sample was ion-sputtered by Ar ions for 0, 30 and 90 min at 3 kV and 80 mA before measurements. The binding energies were calibrated by the C 1s binding energy of 285.0 eV.

The specific surface area of the catalyst was measured by BET method on a Micromeritics ASAP-2010 apparatus at liquid nitrogen temperature with N_2 as the absorbent at 77 K.

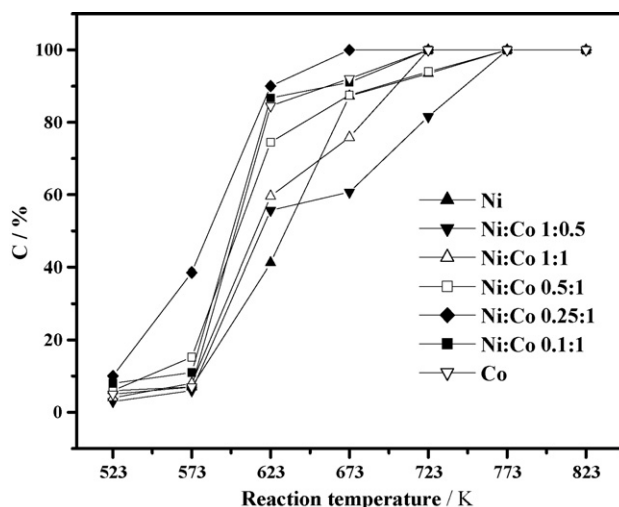


Fig. 1. Influences of the molar ratios of Ni and Co on the conversions of acetic acid. Experimental conditions: S/C mol ratio 7.5:1; LHSV = 5.1 h^{-1} ; $P = 1 \text{ atm}$.

3. Results and discussion

3.1. Effects of the molar ratios between Ni and Co in the catalysts

The molar ratios between Ni and Co in the catalysts were varied in the range from 1:0 to 0:1 and the catalysts were evaluated from 523 to 823 K. The activities of the catalysts were determined in terms of conversions of acetic acid and selectivities to the products as shown in Fig. 1 and Table 1. Based on the results, we found different catalysts had comparable activities at temperature above 773 K. However, below the temperature, the differences became significant, especially at 623 K. It was evident that the activities of the catalysts increased with the increase of Co content and reached maximum at the ratio of 0.25:1 between Ni and Co. And at this ratio, the Ni–Co catalyst not only showed the superior performances at 623 K, but also in the whole temperature range studied. For the steam reforming of acetic acid, single metal Ni and Co catalysts were also active, but it was clear that they were inferior to Ni–Co catalyst (0.25:1), both in terms of conversions of acetic acid and selectivities to the products. It is well known that an effective catalyst for reforming of oxygenate compounds should not only be active for cleavage of C–C bond, but also be active for WGS reaction to remove CO

Table 1
Influences of the molar ratios of Ni and Co on selectivities to the products

Catalysts	$S_{\text{H}_2} (\%)$	$S_{\text{CH}_4} (\%)$	$S_{\text{CO}} (\%)$	$S_{\text{CO}_2} (\%)$
Ni	93.4	3.1	1.2	95.6
Ni:Co (1:0.5)	96.1	1.1	0.21	97.3
Ni:Co (1:1)	95.7	2.2	0	96.8
Ni:Co (0.5:1)	96.2	0.96	0	97.9
Ni:Co (0.25:1)	96.3	0.94	0	98.1
Ni:Co (0.1:1)	95.9	1.5	0	96.7
Co	95.7	1.4	0	96.5

Experimental conditions— $T = 673 \text{ K}$; S/C mol ratio 7.5:1; LHSV = 5.1 h^{-1} ; $P = 1 \text{ atm}$.

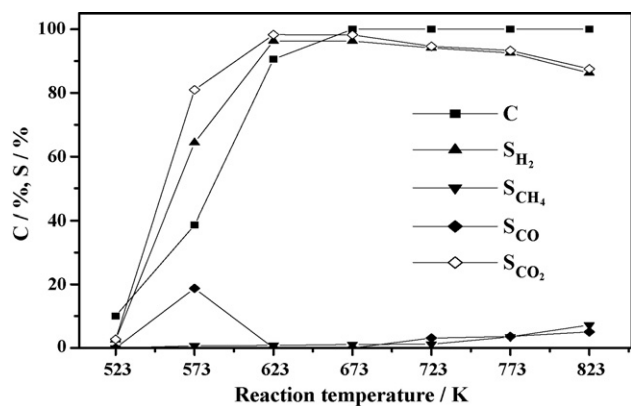


Fig. 2. Effects of temperature on the conversions of acetic acid and selectivities to the products. Experimental conditions—catalyst: Ni–Co (0.25:1); S/C molar ratio 7.5:1; LHSV = 5.1 h⁻¹; P = 1 atm.

formed on metal surface. Sinfelt and Yates [12] reported that C–C bond cleavage is faster over Ni than other group VIII metals. However, Ni had limited activity for WGS reactions [13,14], while Co had relatively higher activities for the reactions [15]. Hence, the integration of Ni and Co in the catalysts can enhance the activity effectively for the reforming of acetic acid. At the ratios of 0.25:1, the catalyst exhibited the best performances. Therefore, this catalyst was conducted in further experiments, such as the influences of reaction temperature, LHSV, S/C, the stability test and the characterizations.

3.2. Effects of reaction temperature

The effects of reaction temperature on the reactions were presented in Fig. 2. It could be observed that reaction temperature had significant influences on acetic acid conversions and selectivities to the products in the narrow temperature range of 573–623 K. At 573 K, the conversion of acetic acid was just 38.6%, but it reached 90.6% with temperature increase to 623 K. At the same time, CO selectivity decreased from 18.7% to nearly 0% sharply, in contrast, the selectivities to H₂ and CO₂ increased dramatically at this condition. The cause of the large amount CO generation at 573 K might be that steam reforming ($\text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 4\text{H}_2$) and water gas shift (WGS: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) reactions could not occur remarkably [16], for acetic acid and steam adsorbed on the surface of the catalyst could not be activated sufficiently due to the low reaction temperature. At 623 K, the steam reforming and WGS reactions proceeded. As a result, both conversions of acetic acid and selectivities to H₂ and CO₂ increased significantly. When the temperature increased consecutively to 673 K, the catalyst exhibited the best performances. Acetic acid was converted completely, and the selectivities to H₂ and CO₂ reached maximum values 96.3% and 98.1%, respectively, while the selectivity to by-product CH₄ was about 0.7% and only negligible amount of CO was detected (~60 ppm). However, when the temperature continuously increased to higher ranges, such as at 823 K, the selectivities to CH₄ and CO became remarkable, while the selectivities toward H₂ and CO₂ decreased to 86.2% and 87.5%, respectively. In addition, there were trace and negligible amount

of acetone detected from 573 to 723 K, hence we did not express it in the figures or tables.

The phenomenon of the increase of selectivity to CH₄ at high temperature was interesting, so a further experiment was carried out. Vannice [17] pointed out that both Ni and Co themselves showed high activity in the methanation of carbon oxides, especially the Co species. Considering that the catalyst studied was Ni–Co and the effluent gas was mainly H₂ and CO₂, we speculated the side reaction of methanation of CO₂ might take place in the reforming process, which might be responsible for the high selectivity to CH₄ in higher temperature ranges. In order to prove this, we conducted the methanation reaction over Ni–Co catalyst under the conditions same as that of steam reforming. The reactants were H₂ and CO₂ and the molar ratio was 2:1 (which was same as the ratio in the effluent gas). The obtained results confirmed our assumptions. There was indeed CH₄ generation at temperature above 573 K and the amounts increased gradually with temperature increase. Appreciable amount CH₄ could be detected in higher temperature ranges. From these results, we concluded that the side reaction of methanation of CO₂ took place in the reforming process, which might be one of the pathways for the generation of CH₄.

One more interesting result in the methanation experiments was that there was CO observed at temperature above 623 K and the amounts increased monotonously with temperature increase. These results indicated that the reverse water gas shift reaction (RWGS: $\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$) occurred. From the point of view in thermodynamic equilibrium and considering that there was steam existed in the reforming reactions, we added some steam to figure out the influence of steam on the RWGS reaction. The observed results consisted with our expectation that steam could depress the generation of CO, only appreciable CO was detected when temperature was higher than 723 K and the amounts decreased considerably compared to the results obtained in the absence of steam. Based on these results, we speculated that the RWGS reaction might be one of the pathways for CO generation in higher temperature ranges, and CO was suppressed to an extent in the presence of steam. Aupretre et al. [14] pointed out that CO was produced from RWGS reaction in steam reforming ethanol. Additionally, negligible CO detected from 623 to 673 K in the reforming reactions implied that WGS reaction might work. We then conducted the WGS reaction over Ni–Co catalyst and observed the catalyst was indeed active, especially at temperature around 623 K. Based on the results of the methanation, RWGS and WGS reactions over Ni–Co catalyst, we concluded that the methanation and RWGS reactions might be the reasons for the high selectivities to CH₄ and CO in higher temperature ranges. And steam was an important factor for depressing the generation of CO, since the WGS reaction was favoured under this condition, while RWGS reaction was suppressed.

3.3. Effects of LHSV

The effects of LHSV on the catalytic performances of Ni–Co catalyst at 673 K were illustrated in Table 2. It can be seen that LHSV had effects on the conversions of acetic acid. With

Table 2
Influences of LHSV on the conversions of acetic acid and selectivities to the products

LHSV (h^{-1})	C (%)	S_{H_2} (%)	S_{CH_4} (%)	S_{CO} (%)	S_{CO_2} (%)
3.3	100	96.0	0.69	0	97.8
5.1	100	96.3	0.67	0	98.1
7.8	99.8	97.3	0.42	0	98.6
9.9	98.1	97.6	0.41	0	98.8
15.6	95.3	97.9	0.38	0	98.9
19.8	92.6	98.1	0.36	0	98.9

Experimental conditions—catalyst: Ni–Co (0.25:1); $T=673$ K; S/C mol ratio 7.5:1; $P=1$ atm.

Table 3
Effects of S/C on the conversions of acetic acid and selectivities to the products at 623 K

S/C	C (%)	S_{H_2} (%)	S_{CH_4} (%)	S_{CO} (%)	S_{CO_2} (%)
7.5:1	90.6	95.4	0.68	0	98.0
5:1	63.1	95.0	1.7	0	96.9
2.5:1	16.7	83.3	8.1	20.4	71.7

Experimental conditions—catalyst: Ni–Co (0.25:1); $T=623$ K; LHSV = 5.1 h^{-1} ; $P=1$ atm.

LHSV increasing from 3.3 to 19.8 h^{-1} , acetic acid conversions decreased from 100% to 92.6%. LHSV also influenced the selectivities to the products. It was very interesting to find that the higher the LHSV, then the lower the selectivity to CH_4 . Obviously, it was unfavourable for CH_4 generation at higher LHSV. The selectivities to H_2 and CO_2 increased slightly for the decreasing of selectivity to CH_4 at higher LHSV. Therefore, we could get higher selectivities to H_2 and CO_2 at higher LHSV with little losing of acetic acid conversions. It was noteworthy that the influence of LHSV on the by-product CO was not observed, since only negligible CO was detected in the whole range of LHSV investigated.

3.4. Effects of S/C molar ratios

The influences of S/C on the reactions were studied at 623 and 723 K, respectively, as shown in Table 3 and Table 4. At 623 K, S/C had significant effects on the conversions of acetic acid, which dropped substantially from 90.6% to 16.7% with S/C decrease from 7.5:1 to 2.5:1. With regard to selectivities to the products, S/C also had remarkable effects, significant amounts of CH_4 and CO were observed at the lower S/C (2.5:1). Generations of CH_4 and CO can greatly affect the selectivity to H_2 ,

Table 4
Effects of S/C on the conversions of acetic acid and selectivities to the products at 723 K

S/C	C (%)	S_{H_2} (%)	S_{CH_4} (%)	S_{CO} (%)	S_{CO_2} (%)
7.5:1	100	94.7	1.6	3.2	94.8
5:1	78.5	93.9	1.9	3.3	94.1
2.5:1	62.1	83.6	8.1	5.8	86.1

Experimental conditions—catalyst: Ni–Co (0.25:1); $T=723$ K; LHSV = 5.1 h^{-1} ; $P=1$ atm.

production of 1 mol of CH_4 will result in 4 mol loss of H_2 , similarly, 1 mol of CO will result in 1 mol loss of H_2 . As a result, when S/C decreased from 5:1 to 2.5:1, the selectivity to H_2 decreased remarkably from 95.0% to 83.3%. In addition, we also studied the influences of S/C at higher temperature 723 K, we found the conversions and selectivities to the products changed significantly (as shown in Table 4). However, at 723 K, the conversions of acetic acid did not dropped remarkably with S/C decrease (see Table 3), in the mean time, the selectivity to CO did not increased obviously. Based on above results, we could figure out the effects of temperature on the reactions at low S/C. The low temperature lead to low steam reforming rates and was unfavourable to shift the equilibrium of WGS to H_2 and CO_2 at low S/C, as a result, low conversions of acetic acid and high selectivity to CO were obtained under this condition. These results were in accordance with the points of Czernik et al. [16].

Wang et al. [9] reported that acetic acid was dissociative adsorption to form CO_x , CH_x ($x=1-2$) and H_{ads} species on the surface of the catalyst in the reforming reactions. Low S/C lead to less adsorption of H_2O molecules, which would inevitably result in less OH_{ads} species on the surface. Consequently, the CH_x species would combine with H_{ads} species to form by-product CH_4 or combine with only one OH_{ads} species then to dehydrogenate to form CO_{ads} species. However, it was difficult to be removed by WGS reaction at low S/C due to the low molar ratios of steam, then another undesired product CO was formed. Therefore, low S/C will affect the adsorption of H_2O molecules and the WGS reaction, which, as a result, lead to the high selectivities to CH_4 and CO. Markevich et al. [6] reported that low S/C resulted in low rate of the steam reforming, owing to the low partial pressure of steam. In another literature, he pointed out that the organic and steam competed in metal sites, and if the active sites on catalyst surface were limited, then the S/C would have much influence on the conversions and distributions of the products [18]. In our study, the characterization showed that Ni–Co catalyst had very limited specific area, which might result in the competence for active sites between acetic acid and H_2O molecules, which then would influence the reactions.

3.5. Stability test

Taking into account that Ni–Co catalyst showed the best performances at 673 K, stability test was carried out at this temperature to insight its catalytic behaviours better. The test performed for 70 h, results were shown in Fig. 3. Acetic acid conversions, and selectivities to the products were plotted as functions of time. It could be seen that Ni–Co catalyst maintained its activity and selectivities for all the time-on-stream under the reaction conditions. The conversions of acetic acid maintained about 100% for all the time studied, while the selectivity to CH_4 increased slightly in the first 30 h, as a result, selectivities to H_2 and CO_2 dropped a little correspondingly, but then the selectivities to the products maintained stable for the rest of time. It was noteworthy that for all the time-on-stream, only negligible CO was detected. Our results indicated that the steam reforming of acetic acid over Ni–Co catalyst could produce almost CO-free hydrogen with high selectivity and stability

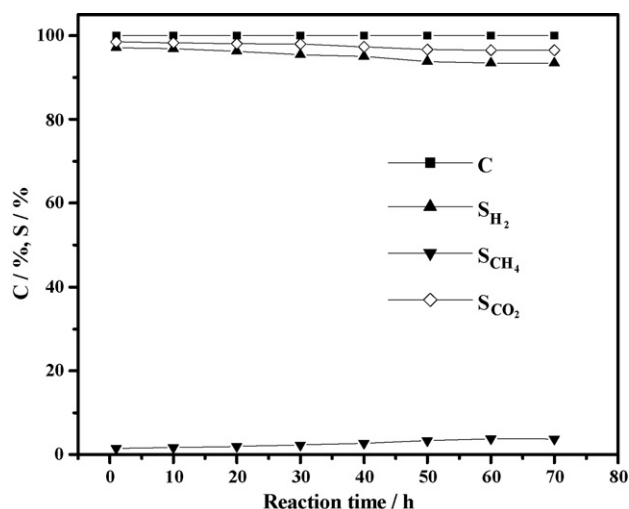


Fig. 3. Stability test for acetic acid reforming over Ni–Co catalyst. Experimental conditions—catalyst: Ni–Co (0.25:1); $T=673$ K; S/C mol ratio: 7.5:1; LHSV: 5.1 h^{-1} ; $P=1$ atm.

at 673 K. Therefore, we thought acetic acid also might be one of the suitable fuels for PEMFC. There are some reports [16,19,20] that hydrocarbons are easily polymerized to form coke on metal sites, which will make the catalyst lost activity. From the above results we found that Ni–Co catalyst had good stability and resistance to carbon deposition at the experimental conditions employed.

We calculated carbon balance by following formula: carbon balance (%) = $100 \times (\text{moles of all the C1 products}) / (\text{moles of acetic acid consumed} \times 2)$. In the stability test, the results show that the carbon balance was higher than 99%. We detected traced amount of acetone and carbon, but these products were less than 1%. We re-measured the catalyst stability and found that catalyst maintained its activity and stability for all time-on-stream. The results indicated that carbon deposition was not serious or the

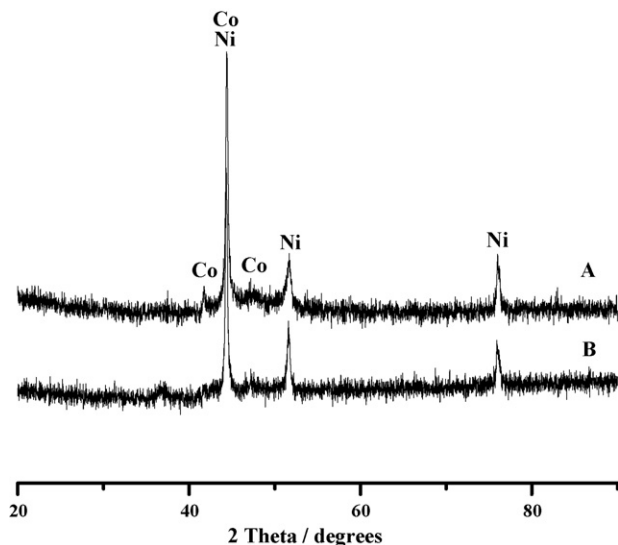


Fig. 4. XRD patterns for the fresh and used Ni–Co catalyst: (A) the fresh catalyst; (B) the used catalyst. Catalyst: Ni–Co (0.25:1).

carbon deposition rate was relatively low at the given reaction conditions.

3.6. Catalyst characterizations

3.6.1. X-ray diffraction

X-ray diffraction patterns for the fresh and used Ni–Co catalysts were presented in Fig. 4. Here the fresh catalyst means that the catalyst is reduced in a hydrogen stream and cooled to a room temperature in a nitrogen stream, while the used catalyst means the tests have been performed. The conditions are: S/C mol ratio 7.5:1; LHSV = 5.1 h^{-1} ; $P=1$ atm and the temperature from 523 to 823 K. It could be seen that the fresh and used catalysts exhibited the comparable diffraction patterns. For the fresh catalyst, the diffraction peaks centred at $2\theta = 41.7^\circ$, 44.4° , and 47.4° , indicated the characteristics of Co phase, while the peaks at 44.4° , 51.6° , and 76.0° indicated Ni phase. For the used catalyst, there were no clear changes of the diffraction peaks. Based on these results we might conclude that no reconstruction of the

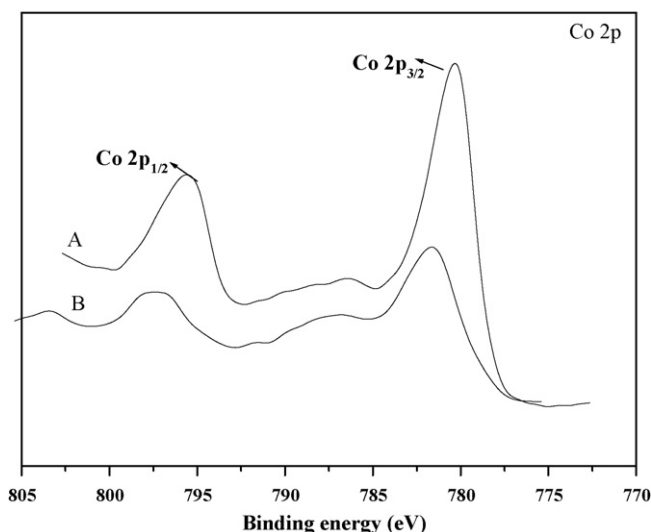
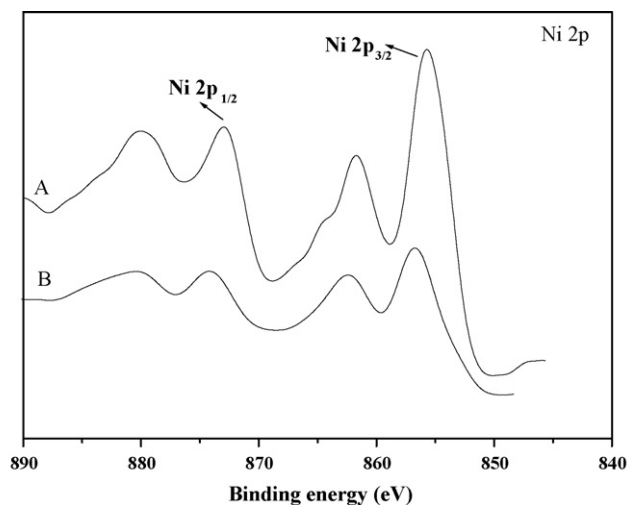


Fig. 5. XPS spectra of Ni 2p and Co 2p for the fresh and used Ni–Co catalysts: (A) the fresh catalyst; (B) the used catalyst. Catalyst: Ni–Co (0.25:1).

sample took place during the process of the reactions. The structure of the catalyst was stable, which was in agreements with the results of the stability test.

3.6.2. XPS characterization

XPS spectra for Ni and Co in the fresh and used catalysts were shown in Fig. 5. For the fresh catalyst, the binding energy of Ni 2p_{3/2} at 855.67 eV was assigned to Ni(II). From the ion-sputter results we knew that the surface metal Ni was oxidized to Ni(II) when exposed to air. The binding energy of the Ni 2p_{3/2} in the used catalyst was 856.68 eV, which should be attributed to Ni(III) [21]. The XPS results of Co were comparable with that of Ni. Co existed as Co(II) with binding energy of Co 2p_{3/2} 780.29 eV in the fresh catalyst, while it became Co(III) in the used catalyst with binding energy of 781.55 eV. The above results indicated that Ni and Co species on the catalyst surface were oxidized during the reactions [22]. Furthermore, the observed binding energies of Ni and Co species were a little higher than the standard data, which could suggested that there existed interactions between them. Based on XPS results, we found the atom concentration change on the catalyst surface. For the fresh catalyst, the molar ratio between Ni and Co was 1:4.5, which was approximately consisted with the theoretical ratio of 1:4, but the ratio became 1:2.7 for the used catalyst, indicating that the Ni species migrated and enriched on the catalyst surface during the reforming reactions.

3.6.3. BET results

The results of BET measurements indicated that the specific area of the Ni–Co catalyst (0.25:1) was very low, just 2.69 m² g⁻¹, and the total volume of pores and average pore diameter were 8.4 × 10⁻³ cm³ g⁻¹ and 7.15 nm, respectively. The Ni–Co catalyst was bimetallic and without support, which might be responsible for the low specific area [23].

4. Conclusion

Summarizing, the present results revealed that the novel Ni–Co catalyst could produce hydrogen via acetic acid steam reforming in relatively low temperature range of 623–823 K effectively. At the molar ratios of 0.25:1 (Ni:Co), the catalyst showed the best performances. LHSV had less effect on the reforming reactions, while reaction temperature and S/C had significant influence on the conversions of acetic acid and distribu-

tions of the products. At $T = 673$ K, $LHSV = 5.1 \text{ h}^{-1}$, $S/C = 7.5:1$, the catalyst exhibited high activity, selectivity and, most importantly, satisfied long-term stability for CO-free hydrogen production. Hence, it was a promising catalyst for acetic acid reforming to generation of hydrogen.

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