

Acetic Acid Steam Reforming over Ni-Fe Catalyst: Complementary Roles of Iron and Reaction Pathways of Methane and CO

HU Xun¹, ZHANG Li-jun², LV Gong-xuan^{1*}

(1. *National Engineering Research Centre for Fine Petrochemical Intermediates, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China;*
2. *Department of Chemistry, Lanzhou University, Lanzhou 730000, China*)

Abstract: Steam reforming of acetic acid for hydrogen generation was investigated over bimetallic Ni-Fe catalysts, monometallic Ni and Fe catalysts to understand behaviours of nickel and iron during the reforming. Monometallic Fe is not active for acetic acid reforming but is important to transform the CO intermediate to H₂ and CO₂. Monometallic Ni is active for acetic acid reforming but is not stable with prolonged reaction time. The combination of these two metals with distinct catalytic capabilities makes the bimetallic Ni-Fe catalyst far superior to the monometallic Ni or Fe catalyst in terms of both activity and stability at the temperature as low as 623 K. The reaction pathways of the two gaseous by-products, methane and CO, were explored as well over the Ni-Fe catalyst. It was found that the 673 K was a critical temperature when the reaction pathways for both methane and CO started to shift. Below 673 K, methane mainly is formed from methanation of CO and CO₂, while above this temperature methane is mainly formed from the decomposition of acetic acid. As for CO, below 673 K, it is mainly formed from the decomposition of acetic acid and the insufficient steam reforming of acetic acid. Above this temperature the reverse water gas shift reaction are the dominate way for CO formation.

Key words: acetic acid; steam reforming; hydrogen; Ni-Fe catalyst; reaction pathways for methane and CO formation

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Hydrogen production from biomass has been recognized as one of the sustainable ways for the production of renewable hydrogen^[1]. In this method, biomass is pyrolyzed first to bio-oil and the followed reforming produce hydrogen^[2-3]. The main challenge during bio-oil steam reforming is the high tendency of bio-oil towards polymerisation. Bio-oil is a very complex mixture of oxygenate compounds ranging from carboxylic acids, sugars, phenolics to the complex oligomers.

The individual behaviours of these components during steam reforming and their specific contribution towards coke formation have not been fully understood yet. Investigation of steam reforming of these major components of bio-oil can help to understand the complex reaction network involved in bio-oil reforming. Carboxylic acids such as acetic acid are one of the ma-

jor components in bio-oil^[4]. Acetic acid is corrosive and is the catalyst for the polymerization of bio-oil^[5]. Understanding how acetic acid behaves during steam reforming can obtain useful information to help to optimize bio-oil reforming process to maximize the hydrogen production while minimize coke formation.

One major challenge during acetic acid reforming is to develop stable and active reforming catalyst at low reaction temperatures to minimize energy input. A number of reforming catalysts have been investigated for acetic acid reforming in recent years^[6-18]. The temperature required to maintain reasonable activity over these catalysts was usually around 873 K, otherwise there were appreciable amounts of by-products generation, which diminishes hydrogen production. To suppress especially the organic by-products such as ketene

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First author: Hu Xun, male, Doctor, E-mail: huxun20032004@126.com(胡勋, 男, 博士, E-mail: huxun20032004@126.com).

* **Corresponding author:** Tel./fax. : +86 931 4968178; E-mail address: gxlu@lzb.ac.cn (G. Lu).

and acetone formation, cracking of the C—C and C—H bonds of acetic acid must be dominate over metals. Nickel is an active metal to crack the organics^[19], and it has been widely used in reforming of organics from simple methanol to the complex bio-oil. In addition to the cracking of organics, the CO intermediates, formed from the cracking reactions or reforming reactions, need to be removed as the form of CO₂ to increase the yields of hydrogen and prevent the formation of coke from CO disproportion. Iron has the capability to catalyze the removal the CO via the water gas-shift reaction^[20].

With the above understanding, we developed a bi-metallic Ni-Fe catalyst with high nickel content to promote the cracking of acetic acid and iron as the second metal to facilitate the water gas shift reaction to remove the adsorbed CO intermediate. The main feature of the catalyst is that it is active, selective and stable for steam reforming of acetic acid at the temperature as low as 623 K, due to the the complementary roles of Ni and Fe species in Ni-Fe catalyst. In addition, the reaction pathways of the CO and CH₄, the two most important gaseous by-products, during acetic acid reforming in the different temperature regions were also investigated.

1 Experimental

Ni-Fe catalyst was prepared by a co-precipitation method. Ni(NO₃)₂ and Fe(NO₃)₃ were used as the metal precursors, which were dissolved and mixed in water. Na₂CO₃ solution was used to co-precipitate the metals by adding it slowly (adding time: 1 h) to the mixed nickel nitrate and iron nitrate solution under vigorously stirring. After finishing adding Na₂CO₃ solution, the resulted product was continuously stirred at room temperature for 24 h. After that, the product was filtered and washed with distilled water until pH was 7, and then dried in air at 383 K for 24 h. The co-precipitated catalyst precursor was then calcined in air at 573 K for 3 h and was crashed to 0.20 ~ 0.56 mm for testing.

X-ray Diffraction patterns (XRD) measurements were performed on a Philips X pert MPD instrument

using Cu Ka radiation in the scanning angle range of 10° ~ 90° at a scanning rate of 4°/min at 40 mA and 50 kV. The specific surface area of the catalyst was measured by BET method on a Micromeritics ASAP-2010 apparatus at a liquid nitrogen temperature with N₂ as the absorbent at 77 K.

Evaluations of the catalysts prepared were carried out in a fixed bed continuous flow quartz reactor operated at atmospheric pressure and in the temperature range from 523 to 823 K. Typically, 0.8 g of calcined catalyst was used in each run and was diluted with equal amount of quartz and was then reduced in situ by 50% H₂ in N₂ stream (flow rate 30 mL / min) at 573 K for 3 h prior to use. The acetic acid/water mixture was introduced into the reactor with a syringe pump. High purity nitrogen was used as the carrier gas and internal standard for gas analysis. The gaseous products were analyzed with two on-line chromatographs equipped with thermal-conductivity detectors (TCD). Unconverted acetic acid and other liquid organic products were analyzed with another GC equipped with a flame ionization detector (FID).

At the end of the catalytic tests, the catalysts were cooled down to room temperature under N₂ and stored for characterizations. Acetic acid conversion and selectivities to the products were calculated to compare their catalytic performances. Selectivities to the products (hydrogen, carbon dioxide, methane, carbon monoxide and so on) were denoted as S_{product} . For example, selectivity to hydrogen was defined as follows: $S_{\text{H}_2}(\%) = 100 \times (\text{moles of H}_2 \text{ production}) / (\text{moles of acetic acid consumed} \times 4)$.

Liquid hourly space velocity (LHSV) was defined as (volumetric flow rate of feed solution (cm³ h⁻¹)) / (catalyst bed volume (cm³)), while ratio of steam to acetic acid (S/C) was defined by the formula: $S/C = (\text{moles of steam in the feed}) / (\text{moles of carbon in the feed})$.

2 Results and discussion

2.1 Effect of Ni and Fe atomic ratio

To identify the optimal Ni and Fe ratios in catalyst for achieving the best catalytic performance, the atomic

ratios between Ni and Fe in catalysts were varied in the range from 1 : 0 to 0 : 1 and the catalysts were evaluated at 623 K. Results were shown in Table 1. Monometallic Ni catalyst showed some activity for acetic acid reforming, but it also showed higher selectivity to CH₄ and CO. Monometallic Fe catalyst was not active for the reforming reaction. Significant amount of acetone, which came from the ketonization of acetic acid, was

detected, leading to rather low H₂ yields. The integration of Ni and Fe in the catalysts significantly improved the catalytic performance, whether in terms of acetic acid conversions and hydrogen yields. Moreover, it was evident that activities of the series of the catalysts increased with the increase of Fe contents and reached the maximum at the atomic ratios of 0.5 : 1 between Ni and Fe.

Table 1 Effects of the atomic ratios between Ni and Fe in the catalysts on acetic acid conversions and product distribution^a

Ni : Fe	C/%	S _{H₂} /%	S _{CH₄} /%	S _{CO} /%	S _{CO₂} /%	S _{Acetone} /%
Ni	40.2	45.7	10.4	20.4	36.9	2.4
1 : 0.5	75.6	73.6	6.6	10.7	74.3	2.1
1 : 1	80.7	85.9	4.3	4.6	88.7	0.8
0.5 : 1	100	92.7	3.7	0.12	95.6	0.14
0.25 : 1	85.7	80.8	3.3	0.42	91.2	1.68
Fe	13.8	12.3	2.1	3.78	20.1	24.5

a. Reaction conditions: *T* = 623 K; *S*/*C* mol ratio 7.5 : 1; *P* = 0.1 MPa.

It is 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 the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) to remove CO formed on metal surface^[21]. Ni is the efficient catalyst for C—C bond cleavage^[22–23]. From Table 1, we do see the conversion of acetic acid is much higher over monometallic Ni than over monometallic Fe. Selectivity towards another organic by-product, acetone, is also much lower over the Ni catalyst than over the Fe catalyst. These results together indicate that the higher activity of nickel for cracking of the organics promotes acetic acid conversion while suppress the formation of the big organics like acetone in the products. However, the selectivity towards CO over the Ni catalyst reaches 20.4%, indicating that the insufficient activity of the catalyst for both steam reforming and the water gas shift reaction. With the addition of Fe to form the catalyst Ni-Fe (1 : 0.5), the catalytic activity improved significantly. The selectivity to CO decreased to half of that over the monometallic Ni catalyst. Fe is the active

species for water gas shift reactions^[24]. Integration of Ni and Fe is more effective to remove the CO formed from acetic acid reforming.

The increased activity for Ni-Fe catalyst (1 : 0.5) is also related to the remarkably bigger specific area ($43.1 \text{ m}^2 \cdot \text{g}^{-1}$) than that of the monometallic Ni catalyst ($21.6 \text{ m}^2 \cdot \text{g}^{-1}$). Bigger specific area indicates more surface area available for the reforming reaction. The lower specific area of the monometallic Ni catalyst is probably because when the nickel nitrate was precipitate, the precipitate formed is relatively uniform. The precipitate from precipitation of nickel nitrate and iron nitrate are not uniform, and created the catalyst precursor with more pores and corresponding bigger specific area. In addition, the difference in terms of stability of Ni-Fe catalyst and the monometallic Ni catalyst is also responsible for the poor performance of the monometallic Ni catalyst. The Ni catalyst deactivated pretty quick with time-on-stream, which will be discussed later.

2.2 Effect of reaction temperature

At the molar ratio of 0.5 : 1 between Ni and Fe, the catalyst exhibited the best catalytic performances. Hence, further investigation of effect of reaction temperature on catalytic performance of this catalyst was conducted. Typical results showing the effect of temperature on the steam reforming of acetic acid over Ni-Fe catalyst were presented in Fig. 1, where acetic acid conversion and selectivities to the products were plotted as functions of reaction temperature. Reaction temperature significantly affect acetic acid conversion and distribution of the products in the narrow temperature range of 523 ~ 623 K. The considerable amount of CO generation at 573 K indicated that steam reforming and the water gas shift reaction could not occur effectively, probably due to the insufficiently activation of acetic acid and the steam absorbed on catalyst surface at the low reaction temperature. At 623 K, the steam reforming and the water gas shift reaction were predominant. Correspondingly, acetic acid was converted completely and the selectivities to H_2 and CO_2 reached the maximum of 92.7% and 95.6%, respectively. Meanwhile, the formation of CO was suppressed substantially. However, with the continuously increasing temperature to higher ranges, the amount of CH_4 and CO in the reformat gas become remarkable, leading to the decrease of H_2 generation.

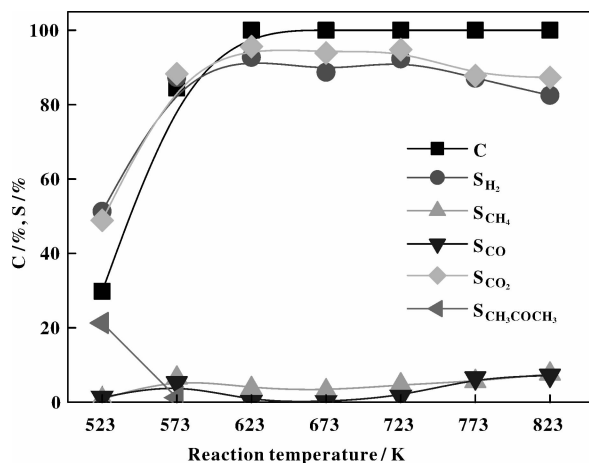


Fig. 1 Effects of temperature on conversion of acetic acid and product distribution

Catalyst: Ni-Fe (0.5 : 1); S/C mol ratio 7.5 : 1;

LHSV = 5.1 h⁻¹; P = 0.1 MPa

During acetic acid steam reforming, ketene, acetone, CH_4 and CO are the main by-products. The formation of ketene and acetone significantly diminish the production of hydrogen. However, their formation is not a serious issue as they can be effectively eliminated via steam reforming by increasing the reaction temperature simply above 623 K. As for CH_4 and CO, in converse, increasing the reaction temperature actually promote their formation. The formation of methane and CO will not only compete for hydrogen formation, but also may lead to the coke formation as they are one of the sources for coke formation. It is very important to understand the detailed reaction pathways for their formation, in order to take corresponding measures to eliminate their production.

2.3 Reaction pathways for the formation of methane and CO

By analyzing the reaction environment, we assumed that methanation and reverse water gas shift reactions are possibly responsible for methane and CO formation, respectively. This is because that Ni-based catalysts showed activity for the methanation of carbon oxides^[25-26]. The catalyst prepared in this study had a high content of Ni and the effluent gas was mainly H_2 and CO_2 . Thus, it was possible that the methanation of CO_2 took place and was responsible for the high selectivity to CH_4 . To prove this hypothesis, The methanation reactions over Ni-Fe catalyst were conducted under the similar experimental conditions (Fig. 2). The

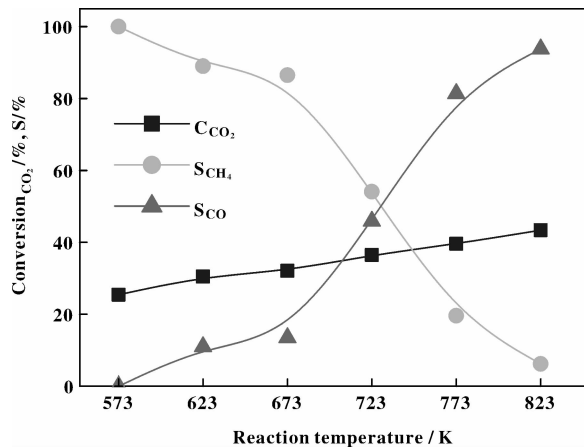


Fig. 2 Activity of the Ni-Fe catalyst for the methanation reaction
Molar ratio of H_2 and CO_2 = 3; GHSV = 3 900 h⁻¹; P = 0.1 MPa

results showed that methanation reaction took place over the catalyst and it was favored only at the temperature below 673 K. At higher reaction temperatures, the methanation reaction was not thermodynamically favored and therefore it has far less contribution to methane formation at the temperature above 673 K. However, in fact methane production increased again with the increase of reaction temperature from 673 to 823 K (Fig. 1). At the high reaction temperature there must be other route that is especially responsible for methane formation. Decomposition of acetic acid can produce methane and carbon dioxides and is promoted at the elevated temperatures. It is highly likely that both the methanation of CO/CO₂ and the decomposition of acetic acid are the main reaction pathways for methane formation. The methanation reaction contributes more to methane formation at the mild temperatures (< 673 K) while that from acetic acid decomposition contributes more to methane formation at the high reaction temperatures (> 673 K).

In addition to the formation of CH₄, it was interesting to observe appreciable amount of CO formed in the methanation reaction at the temperature above 673 K, indicating that the water gas shift reaction occurred in parallel over the catalyst during the steam reforming. Clearly, the reverse water shift reaction contributes to CO formation especially at the elevated reaction temperatures. In acetic acid reforming, CO can be formed via 1): insufficient steam reforming of acetic acid or the insufficient removal of CO via the reverse water gas shift reaction; 2): the decomposition of acetic acid; 3): the reverse water gas shift reaction. From Figure 1 it was shown that the formation of CO experienced a minimum around 673 K. At this temperature the catalyst was activated for steam reforming. As can be seen from Figure 1 where the acetic acid conversion reached 100% and the organic by-product such as acetone also disappear. Correspondingly, the CO formation from acetic acid decomposition and the insufficient steam reforming was suppressed, resulting in formation of much less CO. At the higher reaction temperatures, CO formation increased again, which is due to the dominance

of the reverse water gas shift reaction.

Hereit can be concluded that 673 K is a critical temperature for the shift of the reaction pathways for the formation of both methane and CO. In the temperature region from 523 to 673 K, methane is mainly formed from the methanation of CO and CO₂, while above this temperature methane is mainly formed from the decomposition of acetic acid. In comparison, CO is mainly formed from the decomposition of acetic acid and the insufficient steam reforming of acetic acid below 673 K. Above this temperature the reverse water gas shift reaction is the dominate reaction pathway for CO formation.

2.4 Effects of S/C

S/C ratio is one key parameter in the reforming reactions, effects of which on product distributions were investigated at 623 and 723 K, respectively. The results were summarized in Table 2. Remarkable effects of S/C on distribution of the products from acetic acid reforming were observed. At 623 K, acetic acid conversions decreased progressively with the decrease of S/C, accompanied by the decrease in H₂ and CO₂ production. Conversely, CH₄ and CO production was promoted at the lower S/C. Dissociative adsorption of acetic acid during steam reforming forms CO_x, CH_x ($x = 1 \sim 2$) and H_{ads} species on catalyst surface^[7]. Low steam ratio would inevitably result in less OH_{ads} species formed. Consequently, the CH_x species would have more chance to combine with H_{ads} species, and then desorbed to form CH₄, or combined with only one OH_{ads} species and then dehydrogenate to CO_{ads}. The CO_{ads} was difficult to be removed via the water gas shift reaction at the low S/C, due to the low molar ratios of steam. As a result, another by-product CO formed. Therefore, the low S/C affects the adsorption of steam and the water gas shift reaction, leading to the formation of the by-products. Increasing reaction temperature to 723 K facilitates acetic acid conversion. However, more CO and CH₄ were formed with the decrease of steam ratio in the reactants. Clearly, without adequate steam on catalyst surface, the side reactions dominate and CO/CH₄ formation are inevitable.

Table 2 Effects of *S/C* on on the reforming reactions^a

<i>S/C</i>	<i>T/K</i>	<i>C/%</i>	<i>S</i> _{H₂} <i>/%</i>	<i>S</i> _{CH₄} <i>/%</i>	<i>S</i> _{CO} <i>/%</i>	<i>S</i> _{CO₂} <i>/%</i>
7.5 : 1	623	100	92.7	3.6	0.12	95.6
	723	100	92.3	4.7	1.5	94.8
5 : 1	623	96.4	90.7	4.1	1.1	93.9
	723	100	86.3	5.8	2.9	89.6
2.5 : 1	623	90.1	88.6	4.5	2.3	92.8
	723	100	81.3	8.1	4.3	83.4

a. Reaction conditions; Catalyst; Ni-Fe (0.5 : 1) , LHSV; 5.1 h⁻¹; *P* = 0.1 MPa.

The remarkable effects of *S/C* on acetic acid conversion are also related to the low specific area in catalyst. During steam reforming the organics and steam compete with the metal sites^[27]. *S/C* would be able to impose more influence on catalytic activity and selectivity if the active sites were limited. Ni-Fe catalyst (0.5 : 1) had small specific area (48.9 m² · g⁻¹), which would inevitably result in the competition for active sites between acetic acid and steam, and consequently affects distribution of the product.

2.5 Stability of Ni-Fe catalyst and monometallic Ni catalyst

Stability of Ni-Fe catalyst (0.5 : 1) was examined at 623 K for 100 h. Results were shown in Fig. 3. Ni-Fe catalyst maintained its activity and selectivities at

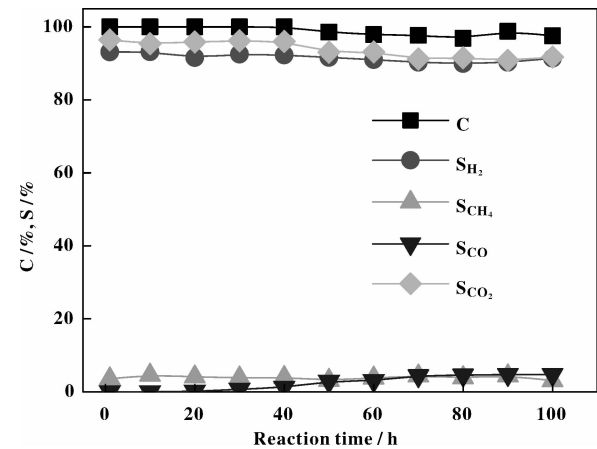


Fig. 3 Stability test for acetic acid reforming over Ni-Fe catalyst
Catalyst; Ni-Fe (0.5 : 1) , *T* = 623 K, *S/C* mol
ratio; 7.5 : 1; LHSV; 5.1 h⁻¹; *P* = 0.1 MPa

the conditions employed. Conversions of acetic acid are

around 100% , and the product distribution was stable in the whole reaction time investigated. During steam reforming coke formation is one of the most possible reasons for the deactivation of reforming catalysts^[28–29]. However, Ni-Fe catalyst showed rather stable activity. The coke formation, determined with TGA, is negligible (ca. 1.3%). The high resistance against carbon deposition is related to the superior activity of the catalyst. Acetic acid was converted completely in the whole time-on-stream and no appreciable organic by-products were produced. Methane and CO are the main by-products. Methane can decompose to form coke while the disproportion of CO can form coke as well. However, the selectivities towards methane and CO are also in a low level (< 5%). Moreover, at 623 K the decomposition of methane is difficult as the temperature is too low for the effective decomposition of methane. Hence, the contribution of methane decomposition towards coke formation is minimized at the reaction temperature used.

Monometallic Ni catalyst also showed some activity for steam reforming of acetic acid even though it is not as active as those bimetallic catalysts. Stability of the monometallic Ni was tested as well, which can provide the information about the contribution of Fe towards stability of the Ni-Fe catalyst from another way. As shown in Fig. 4, the monometallic Ni catalyst lost its reforming activity very rapidly in the initial time-on-stream. The selectivity of hydrogen and the typical reforming by-products, CO and CH₄, also decreased significantly. In comparison, the ketonization product, acetone, increased substantially. Acetone is formed

from the decarboxylic reaction of two molecules of acetic acids. Apparently, the monometallic Ni deactivates, and is not able to catalyze the dissociation of acetic acid. Consequently, polymerization of acetic acid and other organics such as acetone dominate.

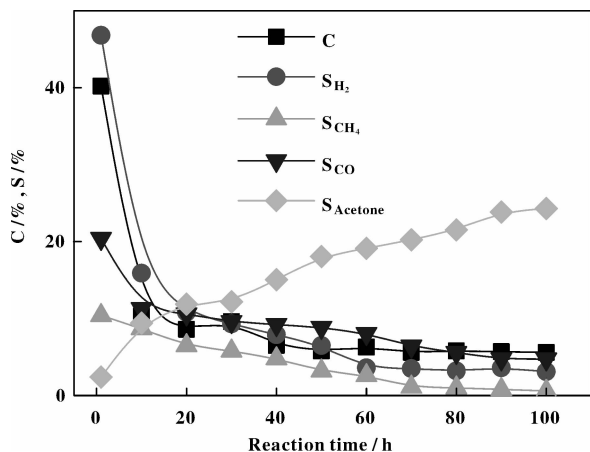


Fig. 4 Stability test for acetic acid reforming over monometallic Ni catalyst

$T = 623 \text{ K}$, $S/C \text{ mol ratio: } 7.5 : 1$;

LHSV: 5.1 h^{-1} ; $P = 0.1 \text{ MPa}$

Deactivation of the Ni species at the thermal conditions would result in the loss of surface active sites and the subsequent production of the by-products, which further promotes the coke formation and the further loss of catalytic activity. The coke formed over the monometallic Ni was ca. 24% to the catalyst loaded, which is much higher than that over the Ni-Fe catalyst. Clearly, Fe is an indispensable ingredient to maintain the stability of the catalyst. Fe itself is the active species in steam reforming, which helps to remove the adsorbed CO species on catalyst surface via water gas shift reaction and increase hydrogen yields. Moreover, Fe can dilute the nickel species on catalyst surface, which may suppress the sintering of nickel species and maintain activity of the catalyst. The presence of Fe in catalyst also enhanced the specific area of the catalysts ($48.9 \text{ m}^2 \cdot \text{g}^{-1}$ of Ni-Fe catalyst versus $21.6 \text{ m}^2 \cdot \text{g}^{-1}$ of monometallic Ni catalyst).

The potential interaction of Fe with Ni during steam reforming of acetic acid was also investigated via characterization of the fresh and used Ni-Fe catalysts

with XRD (Fig. 5). For the fresh catalyst, the diffraction peaks could be identified as NiFe_2O_4 and NiO phases, respectively. The formation of NiFe_2O_4 indicates the interaction of nickel species and iron species during the catalyst preparation and/or the catalyst reduction. In addition, metallic nickel species was not observed in the spectrum, which possibly exists on catalyst surface in a highly dispersed state. As regard the used catalyst, some new diffractions peaks were presented, which centred at $2\theta = 44.3^\circ$, 51.6° and 76.0° , indicating the formation of FeNi_3 alloy phase during the reforming reactions. The formation of the FeNi_3 alloy indicates that some iron oxide was reduced during steam reforming and reacted with metallic nickel species formed the alloy. In addition, the direct reduction of NiFe_2O_4 may also produce the FeNi_3 alloy. The solid-phase reactions between iron and nickel, which result in the formation of new compounds, probably prevent the sintering of nickel species and increase the dispersion of nickel species on catalyst surface.

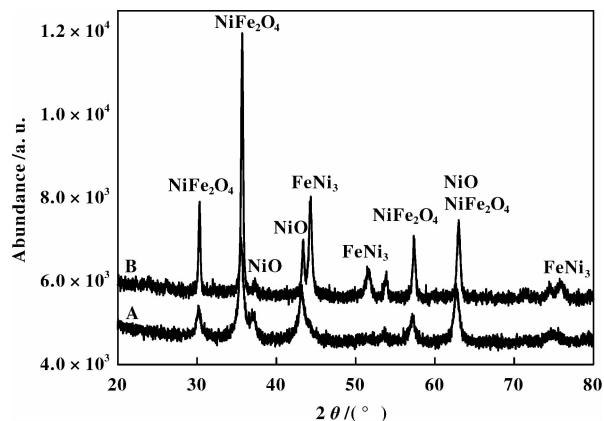


Fig. 5 XRD patterns of fresh and used Ni-Fe catalysts (0.5 : 1)

A: the fresh catalyst (after reduction); B: the used catalyst (after the reforming reactions)

3 Conclusions

In summary, the results presented above revealed that the Ni-Fe bimetallic catalyst (0.5 : 1) is highly active, selective and, most importantly, exhibited good long-term stability for hydrogen production at the temperature as low as 623 K. This bimetallic Ni-Fe catalysts show the superior activity and stability than the

monometallic Fe or monometallic Ni catalysts due to the complementary roles of the two metal species in acetic acid steam reforming. The addition of iron to the Ni-Fe catalyst increased the specific area of the catalyst and promotes the removal of CO via the water gas shift reaction. In addition, 673 K is a critical temperature which changes the reaction pathways for both methane and CO over the Ni-Fe catalyst. Methane is mainly produced from the methanation of the carbon oxides below this temperature, while the methane formation from acetic acid decomposition is dominated at the elevated temperatures. CO is mainly formed from acetic acid decomposition and the insufficient steam reforming of acetic acid below 673 K while the reverse water gas shift reaction are the dominate route for CO formation at the reaction temperature above 673 K. The thermodynamics and the catalyst together determine the formation of these two main gaseous by-products. Rational selection of reaction conditions and reforming catalyst can be integrated to minimize the formation of methane and CO to enhance hydrogen selectivity.

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镍-铁双金属催化剂在乙酸水蒸气重整制氢 反应中的催化性能 ——铁的互补作用和甲烷及 CO 生成的反应路径

胡 勋¹, 张丽君², 吕功煊^{1*}

(1. 中国科学院兰州化学物理研究所 精细石油化工中间体国家工程中心, 甘肃 兰州, 730000;

2. 兰州大学 化学系, 甘肃 兰州, 730000)

摘要: 我们研究了镍-铁双金属催化剂在乙酸水蒸气重整制氢反应中的催化性能. 研究结果显示单金属铁催化剂对乙酸重整反应活性很低, 但是对一氧化碳的中温变换反应有较好的催化性能. 镍单金属催化剂对乙酸水蒸气重整制氢反应有非常好的初始催化活性, 但是催化剂的长期稳定性很差. 镍-铁复合催化剂的低温活性 (623 K) 和长期稳定性 (100 h) 都远好于单金属催化剂. 这主要是因为铁的加入可以促进镍的分散, 形成更多的表面活性位同时有助与防止镍的烧结. 我们也对乙酸重整反应中的两个主要气体副产物 (一氧化碳和甲烷) 的反应路径进行了分析. 研究发现反应温度决定一氧化碳和甲烷的反应路径. 673 K 是一个临界温度. 低于此温度, 甲烷的产生主要来自于一氧化碳和二氧化碳的甲烷化, 而高于 673 K, 甲烷主要来自于乙酸的直接裂解. 对于一氧化碳副产物而言, 低于 673 K 其主要来自于乙酸的裂解或者不充分的水蒸气重整反应, 而高于 673 K 产生的一氧化碳则主要来自与逆水煤气变换反应.

关键词: 乙酸; 蒸汽重整; 制氢; Ni-Fe 催化剂; 甲烷、一氧化碳生成路径