Contents lists available at ScienceDirect

# ELSEVIER



Molecular Catalysis

journal homepage: www.journals.elsevier.com/molecular-catalysis

### Interaction of the reaction intermediates in co-reforming of acetic acid and ethanol impacts coke properties

Zhiran Gao<sup>a</sup>, Guoming Gao<sup>a</sup>, Chao Li<sup>a</sup>, Hongli Tian<sup>a</sup>, Qing Xu<sup>a</sup>, Shu Zhang<sup>b</sup>, Leilei Xu<sup>c</sup>, Xun Hu<sup>a,\*</sup>

<sup>a</sup> School of Material Science and Engineering, University of Jinan, Jinan, 250022, PR China

<sup>b</sup> College of Materials Science and Engineering, Nanjing Forestry University, Nanjing, 210037, PR China

<sup>c</sup> School of Environmental Science & Technology, Nanjing University of Information Science & Technology, Nanjing, 210044, PR China

RTICLE INFO	A B S T R A C T
ywords: eam reforming etic acid hanol eaction intermediate eke	Bio-oil is a mixture of organics and its steam reforming for production of hydrogen has attracted extensive attention. During steam reforming, the reaction intermediates derived from the varied organics in bio-oil might interact with each other, impacting composition/properties of the products. In this study, steam reforming of single or mixture of acetic acid and ethanol, the representatives of carboxylic acid and alcohol, were conducted with Ni/KIT-6 as the catalyst, aiming to probe the potential interaction of the reaction intermediates on the reforming reaction. The results showed that the interactions of the derivatives from acetic acid and ethanol did exist, enhancing conversion of reactants, formation of gaseous by-products and affecting coke properties. The co- reforming of ethanol and acetic acid generates more reaction intermediates bearing hydroxyl group that are difficult to be gasified and also forms more coke, leading to more significant catalyst deactivation. The coke formed from the co-reforming is not only prone to oxidation, but also showed distinct morphologies. Carbon nanotubes with coarse surface and hillocks was the main form of coke from steam reforming of ethanol or acetic

like substance or rope-like structures with no cavity and micrometers of length.

#### 1. Introduction

A Ke St Ac Et Re

Hydrogen is clean fuel for fuel cells and its production has always been a hot research topic since decades ago [1,2]. Hydrogen can be produced from various carbonaceous feedstocks via the processes such as steam reforming [3,4], partial oxidation [5,6], oxidative reforming (gasification) [7,8], etc. The carbonaceous feedstock can be fossil fuels (coal, petroleum-based fuels, natural gas) [9,10], small organics like ethanol [11,12], acetic acid [13,14] and methanol [15,16], the organic mixture like bio-oil [17-19], etc. The availability of the feedstock determines feasibility and sustainability of the process. Fossil fuels are nonrenewable and attention for the production of hydrogen has shifted to the feedstock such as the small organics mentioned above [20-22]. However, the small organics like ethanol is an important raw feedstock for the synthesis of other fine chemicals and can also be directly used as the fuel for vehicles [23,24]. Other renewable while abundantly available feedstock with the low production cost is highly demanded for hydrogen production.

Bio-oil is composed by the condensable volatiles from pyrolysis of the renewable biomass [25,26], which can be abundantly produced and available in most of the regions with the growth of biomass. Therefore, bio-oil has been considered as an important feedstock for hydrogen production and steam reforming of bio-oil has been extensively investigated [27-30]. However, inheriting from the complex nature of biomass, the organics in bio-oil are rather complicated in terms of structures, functionalities, molecular sizes, etc [31-33]. Most importantly, the organics in bio-oil tend to polymerize or crack at the elevated temperature, resulting in formation of coke and rapid deactivation of catalysts [34-36]. The coke formation relates to the reaction behaviors of the individual organic compound in bio-oil [37,38]. Nevertheless, when a mixture of organics is formed simultaneously on the same catalyst, a natural question is raised. Do these molecules of different structures and properties interact with each other? If they do, do the interactions affect their coking tendency and the formation of the reaction intermediates. It is known under the typical reforming conditions, the radicals could form. The varied feedstock would generate the

acid, while coke from the co-reforming was mainly in the form of carbon nanofiber decorated with the hangnail-

https://doi.org/10.1016/j.mcat.2021.111461

Received 29 December 2020; Received in revised form 26 January 2021; Accepted 9 February 2021 Available online 25 February 2021 2468-8231/© 2021 Elsevier B.V. All rights reserved.

<sup>\*</sup> Corresponding author. *E-mail address:* Xun.Hu@outlook.com (X. Hu).



**Fig. 1.** The characterization of physical and chemical properties of calcined catalyst. (a): the XRD characterization of the calcined catalyst and the reduced catalyst; (b): the isothermal curves of BJH desorption hole over the calcined catalyst, the symbol of circle means adsorption isotherm curves and the square means desorption isotherm; (c): volume distribution diagram of BJH desorption hole; (d): the TPR characterization of the calcined catalyst.

radicals of different structures. In theory, these radicals could react with each other and hence the interaction of the reactants of different structures seems inevitable. However, this is still a knowledge gap to be filled to understand the complex reaction network during steam reforming of bio-oil that generally contains hundreds of organics [39–41].

As a proof of concept, in this study, acetic acid and ethanol, which could represent the carboxylic acids and alcohols in bio-oil, are selected as the model compounds to investigate their potential interactions. Particularly, the potential interactions of the reaction intermediates in the co-reforming of acetic acid and ethanol on the properties of the coke formed and the reaction intermediates produced were focused. Since catalyst development is not the aim of this study, a typical reforming catalyst, Ni/ KIT-6 was used for reforming of the organics. The results indicated that the interaction between the reaction intermediate produced from steam reforming of acetic acid and ethanol did exist which significantly impacted the distribution of the products and the properties/morphologies of the coke formed.

#### 2. Experiment

#### 2.1. Preparation of catalyst

KIT-6 was prepared with triblock copolymer (P123) as template, tetraethyl silicate as silicon source and n-butanol as coexisting solute, according to that specified in literature [42]. In the preparation of Ni/KIT-6 catalyst, nickel was loaded on the carrier KIT-6 by an incipient impregnation method. Nickel nitrate was selected as nickel source. A certain amount of nickel nitrate was dissolved in deionized water to obtain nickel nitrate solution. After that, it was mixed with KIT-6, aged

at room temperature for 24 h, and then in an oven of 60 °C for another 24 h. After drying, the solid sample was calcined by heating in static air to 600 °C at the rate of 20 °C/min and holding for 2 h in a muffle furnace to obtain the calcined catalyst.

#### 2.2. Catalytic experiment

The steam reforming of acetic acid, ethanol and their mixture was carried out in a fixed bed continuous flow reactor. The configuration of the reactor could refer to our previous work [43]. 0.5 g of calcined catalyst was loaded in a quartz reactor and was placed in the center of the furnace. Before the start of the reforming reaction, the calcined catalyst was reduced at 600 °C at the heating rate of 20 °C/min for 1 h in the mixed atmosphere of  $H_2/N_2$  ( $H_2 = 60$  mL/min;  $N_2 = 60$  mL/min). The reforming experiment was then started when the reaction temperature was decreased to the preset value. The reactant(s) was pumped into the reaction tube at a flow rate (0.12 mL/min) through a peristaltic pump. In the co-reforming of acetic acid and ethanol, the steam to carbon ratio (S/C) was adjusted to the same as that in steam reforming of the single feedstock. In the mixture, the molar ratios between ethanol and acetic acid was 1:1. In the steam reforming, N2 with a flow rate of 60 mL/min was used as a carrier gas. After holding at each reaction temperature for 30 min, the liquid products were collected by a gas-liquid separator, and the gas products were collected by a gas bag and were analyzed with Gas Chromatography (GC). After the experiment, the spent catalyst was cooled to room temperature under the protection of N2, and was then collected and further analyzed. The calculation formulas for the conversion of the organics and the yields of the gases were as follows.

Conversion =

Amount of acetic acid	/ethanol in feedstock – A	mount of acetic acid/ethanol
-----------------------	---------------------------	------------------------------

in residual

Amount of acetic acid/ethanol in feedstock

$$Yield_{CO/CH_4/CO_2} = \frac{Moles of CO/CH_4/CO_2 produced}{2 \times Moles of acetic acid/ethanol} \times 100\%$$

$$Yield_{H_2} = \frac{Moles of H_2 produced}{Theoretical of H_2 from the acetic acid/ethanol fed in} \times 100\%$$

#### 2.3. Characterization and analytical methods

Brunauer Emmet Teller (BET) surface areas of the catalysts were measured by using the Biaode SSA 6000 instrument, and the phase characteristics of catalysts were analyzed by Powder X ray diffraction (XRD) of Rigaku Ultima IV. The reduction behaviors of nickel oxide were measured (temperature-programmed reduction in hydrogen, H<sub>2</sub>-TPR) by using a chemisorption analyzer of Biaode PCA-1200.

The amount of coke formed was measured by using thermogravimetric analysis (TG) with HCT-1 (Henven) instrument. The functionalities of coke were analyzed by Fourier transform infrared (FT-IR) with the Nicolet IS 50 instrument. The micromorphology of coke and the spent catalyst was obtained by the characterization of with a transmission electron microscope (TEM, JEOL2010plus). The details for the above characterizations were described in our previous studies [44].

#### 3. Result and discussion

#### 3.1. Characterization of catalyst

#### 3.1.1. XRD characterization

The XRD patterns of the calcined catalyst and reduced Ni/KIT-6 catalyst were shown in Fig. 1a. In Fig. 1a, the diffraction peaks with  $2\theta$  of 37.4°, 43.4°, 56.4°, 63.1° and 75.6° belonged to the characteristic diffraction peaks of NiO (JCPD number 65-5745), and the diffraction peaks with 20 angles of 44.5°, 51.9° and 76.5° belonged to the characteristic diffraction peaks of metallic nickel (JCPD number 65-2865). The carrier KIT-6 existed in the form of amorphous SiO<sub>2</sub>, and the characteristic diffraction peak was located at 22.7°. According to Scherrer formula, the grain size of nickel oxide in the calcined catalyst was 12.9 nm and that of nickel metal in the reduced catalyst was 10.3 nm. In theory, if no migration of metallic nickel took place, the particle size of nickel in the metallic form should be even smaller than that of NiO as the removal of oxygen would remarkably decrease the particle sizes. However, the migration and aggregation of nickel species almost cannot be avoided, which relates to both the pore structure of the catalyst and the interaction between the carrier and nickel species. The pore structures of the catalyst were firstly analyzed.

#### 3.1.2. BET characterization

The isothermal curve of calcined catalyst and the volume distribution of BJH desorption pore were shown in Fig. 1b and c, respectively. The specific surface area for the calcined catalyst was  $360.6 \text{ m}^2/\text{g}$ . The average mean radius of the particles was 32.7 Å, and the pore volume was  $0.59 \text{ cm}^3/\text{g}$ . The results in Fig. 1a indicated that the adsorption branch measured with the increase of the equilibrium pressure and the desorption branch measured with the decrease of the pressure did not coincide in a certain relative pressure range, and the type of hysteresis loop belongs to H1 type. The formation of H1 type hysteresis loop was the behavior of cylindrical pores with uniform diameter distribution at both ends in the adsorption and desorption process, which could be



 $\times 100\%$ 

**Fig. 2.** The yield of the main products in the steam reforming of different substrates with the 18 %Ni/KIT-6 as the catalysts. Reaction condition: Catalyst loading: 0.5 g; LHSV =6.9  $h^{-1}$ ; S/C = 5; P =1 atm.



Fig. 3. The In-situ DRIFTS characterization of steam reforming of different reaction substrates. (a): acetic acid; (b): ethanol; (c): mixture of acetic acid and ethanol.

observed in mesoporous materials with uniform size distribution [45]. From the volume distribution diagram, it could be verified again that the pore size of the catalyst was mainly concentrated in the range of 30–35 Å, which belongs to mesoporous materials. Mesoporous materials with high specific surface area could enhance the interaction between the carrier and metal active materials and improved the dispersion of metal, which could maximize the utilization of active materials. In order to further study the interaction between carrier and the nickel species, the TPR characterization was carried out subsequently.

#### 3.1.3. TPR characterization

The TPR characterization results of the calcined catalyst were shown in Fig. 1d. Three main reduction peaks could be seen at 237 °C, 408 °C and 590 °C, respectively. The reduction peak at 237 °C was not obvious and existed in the form of small shoulder peak. The reduction peak at 408 °C had the largest area while the reduction peak at 590 °C was significant in terms of the peak area. The reduction temperature of the unsupported nickel oxide to nickel was generally around 400 °C [46]. The higher reduction temperature indicated stronger interaction between NiO and carrier. In addition, the mass transfer of hydrogen to the inner pores of the catalyst also affects the reduction of NiO inside the pores. The reaction behaviors of ethanol, acetic acid and the mixture of ethanol/acetic acid over the Ni/KIT-6 catalyst was further investigated to explore the interaction of the reaction intermediates in the co-steam reforming reactions.

#### 3.2. Catalytic performance

#### 3.2.1. Catalysis experiment

The gaseous products versus the reaction temperatures with Ni/KIT-

6 as the catalyst in the steam reforming of single ethanol, acetic acid and their mixture were shown in Fig. 2. The higher temperature enhanced the catalytic activity of Ni/KIT-6, facilitating the conversion of acetic acid and ethanol as well as the formation of the gaseous products. Interestingly, acetic acid and ethanol showed the varied reaction behaviors when they were reformed together. An apparent phenomenon was that the conversion of both acetic acid and ethanol (Fig. 2c) was higher than that in steam reforming of the single feedstock. The distribution of the gaseous products was also different in the co-reforming and in the reforming of the single feedstock. For example, the yields of CH<sub>4</sub> were higher with the increased reaction temperature in the co-reforming reactions than that in reforming of the single feedstock. Similar phenomenon was also observed for the production of CO. The production of CH<sub>4</sub> and CO could be originated from the methanation reaction and the reverse water gas shift reaction [47,48], respectively. Nevertheless, they could also be produced from the decomposition of the reactants and the radical reactions between the reaction intermediates. The co-existence of ethanol and acetic acid in the reaction mixture should have induced the interactions of the reaction intermediates, which not only changed the conversion of acetic acid and ethanol, but also significantly impacted the formation of the gaseous products. The reaction intermediates formed in steam reforming of the single or the mixed feedstocks were further characterized with the in situ DRIFTS studies.

## 3.2.2. In situ DRIFTS studies of steam reforming of different reaction substrate

The results of in situ DRIFTS studies of steam reforming of three different reaction substrates were shown in Fig. 3. The infrared characteristic peaks at 2848 cm<sup>-1</sup> and 2932 cm<sup>-1</sup> were –CH<sub>2</sub>, [49], which were the decomposition products of small organic molecules. The



**Fig. 4.** The yield of the main products in the steam reforming of different substrates versus the prolonged reaction time. Reaction conditions: catalyst loading: 0.3 g; LHSV =6.9 h<sup>-1</sup>; S/C: 2; reaction temperature: 600 °C; reaction time: 300 min.

infrared absorption peaks at 2307 cm<sup>-1</sup> and 2384 cm<sup>-1</sup> belonged to the vibration absorption of CO<sub>2</sub>. The stretching vibration of C=O at 1821 cm<sup>-1</sup>, C=H at 2876 cm<sup>-1</sup> and C=C at 1585 cm<sup>-1</sup> were all functional groups formed by the decomposition of organic compounds during the steam reforming. The absorption peak of Si-O-Si at 1000 cm<sup>-1</sup> was caused by the asymmetric stretching and bending vibration of Si-O-Si framework in zeolite. Meanwhile, the infrared peak of Si-O at 770 cm<sup>-1</sup> belonged to KIT-6. According to the statistics of the peak height of

each peak, Table 2 was obtained. With the increase of reaction temperature, the reaction speed was accelerating, and the peak value was also gradually increasing. For the reforming of acetic acid or ethanol, the vibration absorption of CO2 was not found at the low temperature (100-200 °C), but began to appear at 400 °C. Different from the single substrate, the vibration peak of CO<sub>2</sub> appeared in the steam reforming reaction of mixture at the temperature even as low as 300 °C, and the peak intensity was much higher than that of single substrate. The interaction between acetic acid and ethanol made the reforming reaction possible at relatively low temperature. The vibrational absorption of olefin =C-H was more significant in the reforming reaction of acetic acid, but not appeared in the reforming reaction of ethanol, Meanwhile, the peak value was not significant in the mixture. This could be due to that the addition of ethanol could relatively inhibit the formation of olefins from the dissociation of acetic acid, resulting in a decrease in the peak strength of =C-H in the steam reforming of the mixture when compared with that in steam reforming of acetic acid. In addition, in steam reforming of the mixed ethanol and acetic acid, the intensity for the hydroxyl group absorption became more significant. The absorption peak should be largely from the organic reactant as the catalyst and the proportion of water in the reactants remained the same. The higher abundance of the hydroxyl group indicated that the interaction between the reaction intermediates formed the organic species with the abundant hydroxyl group and they were more difficult to be gasified. They could be the precursor of coke.

The peak value of  $-CH_x$  was the lowest in the steam reforming of the mixture, which may be due to the further conversion of -CH<sub>x</sub> to CH<sub>4</sub>, as the higher yield of CH<sub>4</sub> was obtained in steam reforming of the mixture (Fig. 2). Similarly, compared with the steam reforming of single reactant, the peak value of vibration absorption peak of CO was higher and the yield of CO was the highest in the mixture reforming, suggesting that the interaction between acetic acid and ethanol probably promoted the formation of CO. The functional groups C-O-C, C=O and C=C all came from the decomposition and further combination of organic compounds. The increase of reaction temperature enhanced the abundance of these functional groups increased, as the steam reforming was accelerated. When the reaction temperature was 600 °C, it was found that the peak value of the three functional groups in ethanol was the highest, while the peak value in the mixture decreased. This further indicated the interaction between acetic acid and ethanol, and also the interaction between the reaction intermediates modified the reaction intermediates. In order to further explore the impacts of steam reforming of the mixed ethanol and acetic acid on the formation of coke, the steam reforming of the single and the mixed feedstock versus the prolonged reaction time was carried out.

#### 3.2.3. Steam reforming versus the prolonged reaction time

The conversion of the reactants and the yields of gas products versus the prolonged reaction time at the reaction temperature of 600 °C and the S/C of 2 were shown in Fig. 4. In the steam reforming of acetic acid, although the conversion of acetic acid was relatively stable with the extension of time-on-stream, the percentage for the decrease of H2 at the end of the experiment was 28.6 % (Fig. 4a). The deactivation of the catalyst probably led to the conversion of acetic acid to the organic byproducts, diminishing the production of H<sub>2</sub>. In the steam reforming of ethanol, deactivation of the catalyst was also observed, as evidenced by the decrease the yield of H<sub>2</sub> by 25 % (Fig. 4b). In the steam reforming of ethanol and acetic acid mixture (Fig. 4c), the catalyst deactivation was obvious, and the deactivation degree was far greater than that of single organic compounds. After 5 h of time-on-stream, the yield of H<sub>2</sub> decreased by 44 %. In addition, the production of CO and CH<sub>4</sub> in the steam reforming of the mixture was higher than that in steam reforming of the single substrate. This once again verified the interaction between acetic acid and ethanol or their derived reaction intermediates in the reforming process affected the reaction network and the formation of gas products. Furthermore, the amount of coke formed in the reforming



**Fig. 5.** The various characterizations of the spent catalysts in the steam reforming of the different substrates versus the prolonged reaction time. (a): the TG-air curves; (b): the DTG-air curves; (c) TPO curves; (d): the FT-IR curves; (e): the TG- $N_2$  curves; (f): the DTG curves in the  $N_2$  atmosphere; (g) the XRD characterizations of the spent catalysts after the catalytic experiment (from Fig. 2); (h) the XRD characterizations of the spent catalysts after the 5 h of time on stream (from Fig. 4).

of the single feedstock and the mixture should also be different, as the catalyst deactivated to the different extent in terms of the yields of hydrogen. This was further investigated via a series of characterization of the spent catalysts to explore the influence of the co-reforming on coke formation and the properties of coke.

#### 3.3. Characterization of the spent catalyst

#### 3.3.1. TG-air and TPO characterization

The TG-air characterizations of the three spent catalysts in an air flow were shown in Fig. 5a. The mass of the three spent catalysts started to increase from ca. 300 °C, which was attributed to the oxidation of nickel in the reduced catalysts in the air stream. When the temperature reached ca. 500 °C, the oxidation of the coke deposit started, resulting in

#### Table 1

The nickel metallic particle size of the different catalysts.

Catalysts	After catalytic experiment <sup>a</sup> / nm	After stability test <sup>b</sup> / nm		
Ni/KIT-6	12.9 <sup>c</sup> /10.3 <sup>d</sup>			
Acetic acid reforming	13.0	13.5		
Ethanol reforming	14.2	14.2		
The mixture	13.4	12.9		
reforming				

<sup>a</sup> The conditions for the catalytic tests were specified in Fig. 2.

 $^{\rm b}\,$  The conditions for the stability tests were specified in Fig. 4.

<sup>c</sup> Means the particle size of nickel oxide in calcined catalyst.

<sup>d</sup> Means the metallic nickel in reduced catalyst.

a sharp downward trend of the TG curves. According to the calculation, 13.3 % of coke in steam reforming of ethanol, 23.1 % coke in steam reforming of acetic acid, and 24.9 % of coke in steam reforming of the mixture were deposited in the spent catalysts. Assuming that there was no interaction between acetic acid and ethanol in the reforming process, the total carbon deposition of steam reforming of the mixture of acetic acid and ethanol with the molar ratio of 1:1 should be half of that of acetic acid and ethanol, which was 18.2 %. However, the actual amount of coke formed in the spent catalyst obtained from the steam reforming of the mixture was 24.9 %, which was an 36.8 % increase the theoretical calculation value. It was confirmed herein again that, in the steam reforming of acetic acid and ethanol mixture, the interaction of the reaction intermediates led to the formation of significantly more coke deposit. The DTG curves in Fig. 5b indicated that the coke deposit formed in steam reforming of ethanol was more resistant to oxidation and followed by that in steam reforming of acetic acid. The coke formed in the co-reforming, however, was prone to oxidation. This again confirmed that the properties of the coke formed in steam reforming of the single feedstock were different from that formed in the co-reforming of the mixture. The oxidation behaviors of the catalyst were further investigated with the TPO characterizations, as shown in Fig. 5c. The oxidation peak formed at lower temperature might be attributed to the oxidation of amorphous coke. The oxidation peak formed at the higher temperature was more significant, which might be due to the oxidation

#### Table 2

The intensity value of absorption peaks in in-situ DRIFTS spectrum.<sup>a</sup>

of some carbon nanotubes with higher graphitization degree. Similarly, the main oxidation temperature of the coke formed from steam reforming of the mixed ethanol and acetic acid was lower. The thermal stability properties of coke generated from steam reforming of single feedstock and coke formed by steam reforming of mixture gas were different.

#### 3.3.2. $TG-N_2$ characterization

The results of thermogravimetric characterization of spent catalyst in nitrogen atmosphere were shown in Fig. 5e and f. With the increase of temperature, the weight loss of spent catalyst began to appear at 210 °C, indicating that some components of the spent catalyst began to decompose. When the temperature finally reached 800 °C, the order of weight loss of spent catalyst was acetic acid > ethanol > mixed acetic acid and ethanol. The weight loss rate was directly related to the stability of carbon deposition. The higher the weight loss rate is, the lower the thermal stability of carbon deposition is. Therefore, it was consistent with the thermal stability of coke obtained by TPO (Fig. 5c). In the reforming of acetic acid, the proportion of vaporized coke to total coke was 35.3 % and 27.3 % in ethanol. The difference between them was relatively small. In the reforming of mixed acetic acid and ethanol, the proportion of vaporized coke was 57.0 %, which was obviously different from that of single material. This further proved that there was interaction between acetic acid and ethanol in the mixture, which affected the specific gravity of vaporized coke and the structure of coke.

#### 3.3.3. XRD and FT-IR characterization

The XRD patterns of the spent catalysts collected were shown in Fig. 5g and h, respectively. The diffraction peaks with  $2\theta$  of  $44.5^{\circ}$ ,  $51.9^{\circ}$  and  $76.5^{\circ}$  were the characteristic diffraction peaks of Ni (JCPD 65–2865). The bulge at the  $2\theta$  of ca.  $21^{\circ}$  was amorphous SiO<sub>2</sub>. In addition, the bulge of carbon was observed at the position of grain size of nickel in the spent catalysts calculated with Scherrer formula was shown in Table 1. Comparing with the nickel particle size in the reduced catalyst, the nickel particle size in the spent catalyst normality in steam reforming of single ethanol. However, in steam reforming of the mixture, the increase of the nickel particle size

Reforming reaction	T∕°C	CO <sub>2</sub> / 10 <sup>-2 b</sup>	=C-H/ 10 <sup>-2c</sup>	$CH_2/10^{-2}$ d	C—O—C/ 10 <sup>-2</sup> e	CO/ $10^{-2 \text{ f}}$	C=O/ 10 <sup>-2 g</sup>	C=C/10 <sup>-2 h</sup>	0—H / 10 <sup>-2 i</sup>
Acetic acid	100		0.1	3.9	0.85	0.8	0.07	13.0	20.4
	200		6.8	5.2	4.0	1.1	1.2	13.6	21.8
	300		6.9	5.6	9.3	1.7	2.6	14.5	22.7
	400	1.3	7.0	6.0	11.6	2.1	4.0	14.9	25.22
	500	1.4	7.4	6.4	18.7	2.6	4.9	15.0	27.6
	600	1.7	9.0	6.7	25.5	2.9	5.7	15.2	30.9
Ethanol	100			1.0	3.9	0.3	0.7	19.9	13.5
	200			1.4	7.1	1.0	1.8	23.7	22.9
	300			1.6	13.7	1.3	3.2	24.4	28.9
	400	0.3		1.9	14.8	1.4	4.0	24.6	30.0
	500	2.4		3.0	24.4	1.4	5.0	25.1	31.6
	600	3.0		4.5	37.1	1.5	6.1	26.4	33.4
Mixture	100		1.5	1.3	4.6	1.1	0.43	3.3	11.5
	200		1.7	1.6	4.7	1.4	1.4	12.1	13.9
	300	1.6	1.8	1.9	6.7	1.7	2.2	17.2	16.9
	400	4.1	2.1	2.1	11.4	3.1	3.3	18.3	20.0
	500	5.0	2.6	2.3	15.7	4.5	4.7	18.0	22.2
	600	5.1	3.7	2.3	25.1	4.9	5.7	19.8	24.4

<sup>a</sup> The data was derived from the results in Fig. 3.

 $^{\rm b}\,$  The absorption peak of CO\_2 was calculated at ca. 2384 cm  $^{-1}.$ 

<sup>c</sup> The absorption peak of  $\equiv$ C-H was calculated at ca. 2876 cm<sup>-1</sup>.

<sup>d</sup> The absorption peak of  $CH_2$  was calculated at ca. 2932 cm<sup>-1</sup>.

<sup>e</sup> The absorption peak of C-O-C was calculated at ca. 1267 cm<sup>-1</sup>.

 $^{\rm f}$  The absorption peak of CO was calculated at ca. 1921 cm<sup>-1</sup>.

 $^{\rm g}$  The absorption peak of C=O was calculated at ca. 1821 cm $^{-1}$ 

<sup>h</sup> The absorption peak of C $\equiv$ C was calculated at ca. 1585 cm<sup>-1</sup>.

<sup>i</sup> The absorption peak of O—H was calculated at ca. 3739 cm<sup>-1</sup>.



Fig. 6. The TEM characterization of the spent catalysts in the steam reforming of the acetic acid versus the prolonged reaction time.



Fig. 7. The TEM characterization of the spent catalysts in the steam reforming of the ethanol versus the prolonged reaction time.



Fig. 8. The TEM characterization of the spent catalysts in the steam reforming of the mixed ethanol and acetic acid versus the prolonged reaction time.

was smaller. This might also due to the coverage of nickel phase with the coke deposit by the different extent, which was further investigated.

The information of the functional groups of the three different spent catalysts and fresh catalysts was shown in Fig. 5d. The characteristic peak at about 3450 cm<sup>-1</sup> corresponded to the vibration absorption of OH of the coke species and/or the adsorbed water. The absorption peaks of C—H and C—O—C were observed at 2919 cm<sup>-1</sup> and 1381 cm<sup>-1</sup>, respectively, indicating that the catalyst contained some aliphatic carbon structures. In addition, the C—C absorption was observed at 1618 cm<sup>-1</sup>, which probably belonged to the aromatic ring structure. The infrared peak at 1085 cm<sup>-1</sup> was caused by the asymmetric stretching and bending vibration of the framework of silica tetrahedron, while the infrared peak at 805 cm<sup>-1</sup> corresponded to the crystal structures and the functionalities of the spent catalysts, the morphologies of the coke formed were further analyzed with the TEM characterizations.

#### 3.3.4. TEM characterization

The results for morphologies of the coke in the spent catalysts were shown in Figs. 6–8, respectively. In the steam reforming of acetic acid, many carbon nanotube structures can be found. Nickel particles located on top of the nanotubes. Some of the nanotubes have a big opening, which was probably due to the fall off of the nickels during the preparation of the samples for the characterization. Depending on the particle sizes of metallic nickel, the diameters of the carbon nanotubes varied remarkably. In addition, the outer surface of the carbon nanotubes was not smooth with many hillocks. Some coke deposits did not grow to form carbon nanotubes, which might be the non-catalytic coke deposited on the surface of the nanotubes. In the spent catalyst in steam reforming of ethanol, similar carbon nanotubes were formed, and nickel particles were also formed on the top of the nanotubes. The formation mechanism of the nanotubes should be similar. In addition, some amorphous coke that covered the surface of the catalyst was always observed. Basically, carbon nanotubes were the main form of coke in the spent catalysts in steam reforming of single acetic acid and single ethanol, which explains the high resistivity of the coke towards oxidation. However, as for the coke formed in the co-reforming of the mixture of acetic acid and ethanol, the coke deposits of the varied morphologies were observed. As shown in Fig. 8, the carbon nanofiber-like structure was observed. It seems the structure was composed by the pile of the hangnail-like substance. The length could be a few micrometers (Fig. 8a) with the diameters of from 20 to 40 nm. In addition, some rope-like structures with very smooth surface was also observed (Fig. 8c and d). The length could also be several micrometers. The structures were not the carbon nanotubes observed in steam reforming of acetic acid or ethanol. The formation mechanism of these structures was obviously different from that carbon nanotube. The results herein clearly demonstrated that the coreforming of acetic acid and ethanol produced the distinct reaction intermediates, which led to the formation of the carbon deposits of the varied morphologies.

#### 4. Conclusion

In summary, the reaction behaviors of co-reforming of acetic acid and ethanol were compared with that of reforming of single acetic acid or ethanol. The results showed that, in the steam reforming of the mixed ethanol and acetic acid, the interaction of the reaction intermediates produced from the varied feedstock not only changed the conversion of acetic acid and ethanol, but also significantly impacted the formation of the gaseous products. The in-situ DRIFTS studies showed that the interaction between the reaction intermediates formed the organic species with the abundant hydroxyl group that were difficult to be gasified. The carbonyl and the C—O—C functionalities of the reaction intermediates were also distinct from that in steam reforming of the single feedstock. The catalyst also deactivated to the highest extent in steam reforming of the mixed ethanol and acetic acid. The coke formation was 36.8 % higher than the theoretical and averaged value in steam reforming of the single feedstock. In addition, the coke formed from the steam reforming of the mixture was less resistant to oxidation and had a lower thermal stability than that in the steam reforming of the single feedstock. The interaction of the reaction intermediates derived from acetic acid and ethanol also changed morphologies of the coke formed. The coke formed from steam reforming of ethanol or acetic acid was mainly in the form of the carbon nanotubes but the surface was not smooth and coated with hillocks. In comparison, the coke formed in steam reforming of mixed ethanol and acetic acid was in the form of carbon nanofiber-like structure piled with the hangnail-like substance. Some rope-like structures with no cavity in the middle but with very smooth surface and the length of several micrometers was also observed. The formation mechanism of these structures was distinct from those carbon nanotubes from the steam reforming of the single feedstock, due to the interaction of the reaction intermediates derived from the conversion of acetic acid and ethanol under the steam reforming conditions.

#### CRediT authorship contribution statement

**Zhiran Gao:** Conceptualization, Methodology, Investigation, Validation, Writing - original draft, Visualization. **Guoming Gao:** Data curation, Validation, Investigation, Writing - review & editing. **Chao Li:** Software, Investigation, Visualization. **Hongli Tian:** Software, Validation, Investigation. **Qing Xu:** Methodology, Investigation. **Shu Zhang:** Supervision, Project administration. **Leilei Xu:** Supervision, Writing review & editing. **Xun Hu:** Conceptualization, Methodology, Resources, Writing - review & editing, Project administration, Funding acquisition.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51876080), the Program for Taishan Scholars of Shandong Province Government. Collaborative Innovation Center of Technology and Equipment for Biological Diagnosis and Therapy in Universities of Shandong.

#### References

- L. Piola, J. Fernández-Salas, F. Nahra, A. Poater, L. Cavallo, S.P. Nolan, Rutheniumcatalysed decomposition of formic acid: fuel cell and catalytic applications, Mol Catal. 440 (2017) (2017) 184–189, https://doi.org/10.1016/j.mcat.2017.06.021.
- [2] S. Chalk, J. Miller, Key challenges and recent progress in batteries, fuel cells, and hydrogen storage for clean energy systems, J. Power Sources 159 (2006) 73–80, https://doi.org/10.1016/j.jpowsour.2006.04.058.
- [3] T. LeValley, A. Richard, M. Fan, The progress in water gas shift and steam reforming hydrogen production technologies-a review, Int J Hydrogen Energ. 39 (2014) 16983–17000, https://doi.org/10.1016/j.ijhydene.2014.08.041.
- [4] D. Palo, R. Dagle, J. Holladay, Methanol steam reforming for hydrogen production, Chem. Rev. 107 (2007) 3992–4021, https://doi.org/10.1021/cr050198b.
- [5] S. Freni, G. Calogero, S. Cavallaro, Hydrogen production from methane through catalytic partial oxidation reactions, J. Power Sources 87 (2000) 28–38, https:// doi.org/10.1016/S0378-7753(99)00357-2.
- [6] A. Lutz, R. Bradshaw, L. Bromberg, A. Rabinoich, Thermodynamic analysis of hydrogen production by partial oxidation reforming, Int J Hydrogen Energ. 29 (2004) 809–816, https://doi.org/10.1016/j.ijhydene.2003.09.015.
- [7] G. Mitran, S. Chen, D. Seo, Role of oxygen vacancies and Mn<sup>4+</sup>/Mn<sup>3+</sup> ratio in oxidation and dry-reforming over cobalt-manganese spinel oxides, Mol Catal. 483 (2019), 110704, https://doi.org/10.1016/j.mcat.2019.110704.
- [8] M. Alvarez-Galvan, R. Navarro, F. Rosa, Y. Briceño, M. Ridao, J. Fierroa, Hydrogen production for fuel cell by oxidative reforming of diesel surrogate: Influence of ceria and/or lanthana over the activity of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, Fuel 87 (2008) 2502–2511, https://doi.org/10.1016/j.fuel.2008.03.003.

- [9] N. Piatkowski, C. Wieckert, A.W. Weimer, A. Steinfeld, Solar-driven gasification of carbonaceous feedstock—a review, Synth. Lect. Energy Environ. Technol. Sci. Soc. 4 (2011) 73–82, https://doi.org/10.1039/C0EE00312C.
- [10] R. Navarro, M. Peña, J. Fierro, Hydrogen production reactions from carbon feedstocks: fossil fuels and biomass, Chem. Rev. 107 (2007) 3952–3991, https:// doi.org/10.1021/cr0501994.
- [11] C. Diagne, H. Idriss, A. Kiennemann, A. Hydrogen production by ethanol reforming over Rh/CeO<sub>2</sub>–ZrO<sub>2</sub> catalysts, Catal. Commun. 3 (2002) 565–571, https://doi.org/ 10.1016/S1566-7367(02)00226-1.
- [12] V. Klouz, V. Fierro, P. Denton, H. Katz, J. Lisse, S. Bouvot-Mauduit, C. Mirodatos, Ethanol reforming for hydrogen production in a hybrid electric vehicle: process optimization, J. Power Sources 105 (2002) 26–34, https://doi.org/10.1016/ S0378-7753(01)00922-3.
- [13] A. Basagiannis, X. Verykios, Catalytic steam reforming of acetic acid for hydrogen production, Int J Hydrogen Energ. 32 (2007) 3343–3355, https://doi.org/ 10.1016/j.ijhydene.2007.04.039.
- [14] S. Sanches, J. Huertas Flores, M. Paisda Silva, Cu/ZnO and Cu/ZnO/ZrO<sub>2</sub> catalysts used for methanol steam reforming, Mol Catal. 454 (2018) 55–62, https://doi.org/ 10.1016/j.mcat.2018.05.012.
- [15] Y. Lwin, W. Daud, A. Mohamad, Z. Yaakob, Hydrogen production from steam-methanol reforming: thermodynamic analysis, Int J Hydrogen Energ. 25 (2000) 47–53, https://doi.org/10.1016/S0360-3199(99)00013-0.
- [16] C. Yao, L. Wang, Y. Liu, G. Wu, Y. Cao, W. Dai, H. He, K. Fan, Effect of preparation method on the hydrogen production from methanol steam reforming over binary Cu/ZrO<sub>2</sub> catalysts, Appl Catal A-Gen. 297 (2006) 151–158, https://doi.org/ 10.1016/j.apcata.2005.09.002.
- [17] P. Kechagiopoulos, S. Voutetakis, A. Lemonidou, I. Vasalos, Hydrogen production via steam reforming of the aqueous phase of Bio-Oil in a fixed bed reactor, Energ Fuel. 20 (2006) 2155–2163, https://doi.org/10.1021/ef060083q.
- [18] W. Nabgan, T. Abdullah, R. Mat, B. Nabgan, Y. Gambo, M. Ibrahim, A. Ahmad, A. Jalil, S. Triwahyono, I. Saeh, Renewable hydrogen production from bio-oil derivative via catalytic steam reforming: an overview, Renew Sust Energ Rev. 79 (2017) 347–357, https://doi.org/10.1016/j.rser.2017.05.069.
- [19] S. Chattanathan, S. Adhikari, N. Abdoulmoumine, A review on current status of hydrogen production from bio-oil, Renew Sust Energ Rev. 16 (2012) 2366–2372, https://doi.org/10.1016/j.rser.2012.01.051.
- [20] S. Yoo, S. Park, J. Song, D. Kim, Hydrogen production by the steam reforming of ethanol over K-promoted Co/Al<sub>2</sub>O<sub>3</sub>-CaO xerogel catalysts, Mol Catal. 491 (2020), 110980, https://doi.org/10.1016/j.mcat.2020.110980.
- [21] Y. Wang, C. Wang, M. Chen, Z. Tang, Z. Yang, J. Hu, H. Zhang, Hydrogen production from steam reforming ethanol over Ni/attapulgite catalysts-Part I, Fuel Process Technol. 192 (2019) 227–238, https://doi.org/10.1016/j. fuproc.2019.04.031.
- [22] Y. Wang, Z. Zhang, S. Zhang, Y. Wang, S. Hu, J. Xiang, X. Hu, Steam reforming of acetic acid over Ni/biochar catalyst treated with HNO<sub>3</sub>: Impacts of the treatment on surface properties and catalytic behaviors, Fuel. 278 (2020), 118341, https:// doi.org/10.1016/j.fuel.2020.118341.
- [23] M. Siqueira, O. Perrone, G. Metzker, D. Lisboa, J. Thoméo, M. Boscolo, Highly selective 1-butanol obtained from ethanol catalyzed by mixed metal oxides: reaction optimization and catalyst structure behavior, Mol Catal. 476 (2019), 110516, https://doi.org/10.1016/j.mcat.2019.110516.
- [24] M. Balat, H. Balat, Recent trends in global production and utilization of bio-ethanol fuel, Appl. Energ. 86 (2009) 2273–2282, https://doi.org/10.1016/j. appnergy.2009.03.015.
- [25] D. Mohan, C. Pittman Jr., P. Steele, Pyrolysis of wood/biomass for bio-oil: a critical review, Energ Fuel. 20 (2006) 848–889, https://doi.org/10.1021/ef0502397.
- [26] D. Carpenter, T. Westover, S. Czernik, W. Jablonski, Biomass feedstocks for renewable fuel production: a review of the impacts of feedstock and pretreatment on the yield and product distribution of fast pyrolysis bio-oils and vapors, Green Chem. 16 (2014) 384–406, https://doi.org/10.1039/C3GC41631C.
- [27] R. Trane, S. Dahl, M. Skjøth-Rasmussen, A. Jensen, Catalytic steam reforming of bio-oil, International Journal of Hydrogen Energy, Int J Hydrogen Energ. 37 (2012) 6447–6472, https://doi.org/10.1016/j.ijhydene.2012.01.023.
- [28] C. Wu, Q. Huang, M. Sui, Y. Yan, F. Wang, Hydrogen production via catalytic steam reforming of fast pyrolysis bio-oil in a two-stage fixed bed reactor system, Fuel Process Technol. 89 (2008) 1306–1316, https://doi.org/10.1016/j. fuproc.2008.05.018.
- [29] T. Chen, C. Wu, R. Liu, Steam reforming of bio-oil from rice husks fast pyrolysis for hydrogen production, Bioresource Technol. 102 (2011) 9236–9240, https://doi. org/10.1016/j.biortech.2011.07.033.
- [30] H. Xie, Q. Yu, Z. Zuo, Z. Han, X. Yao, Q. Qin, Hydrogen production via sorptionenhanced catalytic steam reforming of bio-oil, Int J Hydrogen Energ. 41 (2016) 2345–2353, https://doi.org/10.1016/j.ijhydene.2015.12.156.
- [31] E. Rodríguez-Aguado, A. Infantes-Molina, D. Ballesteros-Plata, J. Cecilia, I. Barroso-Martín, E. Rodríguez-Castellón, Ni and Fe mixed phosphides catalysts for O-removal of a bio-oil model molecule from lignocellulosic biomass, Mol Catal. 437 (2017) 130–139, https://doi.org/10.1016/j.mcat.2017.05.008.
- [32] S. Xiu, A. Shahbazi, Bio-oil production and upgrading research: a review, Renew Sust Energ Rev. 16 (2012) 4406–4414, https://doi.org/10.1016/j. rser.2012.04.028.
- [33] D. Chen, J. Zhou, Q. Zhang, X. Zhu, Evaluation methods and research progresses in bio-oil storage stability, Renew Sust Energ Rev. 40 (2014) 69–79, https://doi.org/ 10.1016/j.rser.2014.07.159.
- [34] X. Hu, Z. Zhang, M. Gholizadeh, S. Zhang, H. Chun, Z. Xiong, Y. Wang, Coke formation during thermal treatment of bio-oil, Energ Fuel. 34 (2020) 7863–7914, https://doi.org/10.1021/acs.energyfuels.0c01323.

- [35] X. Li, Z. Zhang, L. Zhang, H. Fan, L. Xu, Q. Liu, S. Wang, X. Hu, Investigation of coking behaviors of model compounds in bio-oil during steam reforming, Fuel. 265 (2020), 116961, https://doi.org/10.1016/j.fuel.2019.116961.
- [36] D. Yao, C. Wu, H. Yang, Q. Hu, M. Nahil, H. Chen, P. Williams, Hydrogen production from catalytic reforming of the aqueous fraction of pyrolysis bio-oil with modified Ni–Al catalysts, Int J Hydrogen Energ. 39 (2014) 14642–14652, https://doi.org/10.1016/j.ijhydene.2014.07.077.
- [37] Z. Li, X. Hu, L. Zhang, S. Liu, G. Lu, Steam reforming of acetic acid over Ni/ZrO<sub>2</sub> catalysts: effects of nickel loading and particle size on product distribution and coke formation, Appl Catal A-Gen. 417 (2012) 281–289, https://doi.org/10.1016/ i.apcata.2012.01.002.
- [38] S. Wauters, G. Marin, Kinetic modeling of coke formation during steam cracking, Ind. Eng. Chem. Res. 41 (2002) 2379–2391, https://doi.org/10.1021/ie010822k.
- [39] L. Zhang, R. Liu, R. Yin, Y. Mei, Upgrading of bio-oil from biomass fast pyrolysis in China: a review, Renew Sust Energ Rev. 24 (2013) 66–72, https://doi.org/ 10.1016/j.rser.2013.03.027.
- [40] Z. Tang, Q. Lu, Y. Zhang, X. Zhu, Q. Guo, One step bio-oil upgrading through hydrotreatment, esterification, and cracking, Ind. Eng. Chem. Res. 48 (2009) 6923–6929, https://doi.org/10.1021/ie900108d.
- [41] S. Ren, X. Ye, A. Borole, Separation of chemical groups from bio-oil water-extract via sequential organic solvent extraction, J Anal Appl Pyrol. 123 (2017) 30–39, https://doi.org/10.1016/j.jaap.2017.01.004.
- [42] L. Xu, C. Wang, J. Guan, Preparation of acid-base bifunctional mesoporous KIT-6 (KIT: Korea Advanced Institute of Science and Technology) and its catalytic

performance in Knoevenagel reaction, J. Solid State Chem. 213 (2014) 250–255, https://doi.org/10.1016/j.jssc.2014.03.010.

- [43] Z. Gao, Z. Zhang, H. Tian, Q. Xu, Z. Xu, B. Li, Q. Liu, C. Li, G. Chen, X. Hu, Ordinary clay as a support of nickel catalyst for steam reforming of acetic acid: impacts of pretreatments of clay on catalytic behaviors, Int J Energ Res. 44 (2020) 10378–10393, https://doi.org/10.1002/er.5660.
- [44] X. Li, Z. Zhang, L. Zhang, G. Gao, T. Wei, Z. Zhang, S. Zhang, G. Chen, C. Li, X. Hu, Availability of steam impacts coke properties in steam reforming of acetic acid, Int J Hydrogen Energ (2020), https://doi.org/10.1016/j.ijhydene.2020.11.269.
- [45] P. Monson, Understanding adsorption/desorption hysteresis for fluids in mesoporous materials using simple molecular models and classical density functional theory, Microporous Mesoporous Mater. 160 (2012) 47–66, https://doi. org/10.1016/j.micromeso.2012.04.043.
- [46] B. Janković, D. Adnađević, S. Mentus, The kinetic study of temperatureprogrammed reduction of nickel oxide in hydrogen atmosphere, Chem. Eng. Sci. 63 (2008) 567–575, https://doi.org/10.1016/j.ces.2007.09.043.
- [47] R. Hayes, W. Thomas, K. Hayes, A study of the nickel-catalyzed methanation reaction, J. Catal. 92 (1985) 312–326, https://doi.org/10.1016/0021-9517(85) 90266-0.
- [48] C. Chen, W. Cheng, S. Lin, Mechanism of CO formation in reverse water–gas shift reaction over Cu/Al<sub>2</sub>O<sub>3</sub> catalyst, Catal Lett. 68 (2000) 45–48. https://link.springer. com/article/10.1023/A:1019071117449.