Towards understanding the carbon catalyzed CO_2 reforming of methane to syngas

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ABSTRACT

In this paper, a fixed-bed reactor is used to study the influence of different conditions on carbon catalyzed CO_2–CH_4 reforming. The surface structure and functional groups of carbonaceous material have been characterized through SEM, XPS, XRD, BET and chemical titration before and after the reaction. Studies have revealed that under non-catalytic condition, methane pyrolysis happens first, followed by the gasification reaction between CO_2 and carbon deposit produced from the pyrolysis. While with carbonaceous material, CO_2 gasification, methane pyrolysis and CO_2–CH_4 reforming can take place at the same time, with the reforming as the main reaction, CO_2 gasification and methane pyrolysis as the side reaction. Catalytic activity varies from one carbonaceous material to another, but their reaction trend is the same on the whole. Those high specific surface area carbonaceous materials show higher catalytic activity. The increase in reaction temperature and residence time of the reforming can improve the conversion of reactant gas. Adjusting the partial pressure of methane can control carbon–hydrogen ratio of the synthesis gas. XPS and XRD characterizations demonstrate that the structural ordering of carbonaceous materials becomes a little messier after the reforming reaction, and the number and content of oxygen functional groups decrease. That means these oxygen functional groups on the surface of carbonaceous materials are involved in the reforming and these groups along with pore structure on the surface are the major factors influencing the catalytic properties. Different oxygen species make the nature of electrical energy on the surface different; the catalytic activity depends on the polarity of oxygen from different species. Those whose polarity is strong have strong activity. The dipole force can be associated with methane in the form of hydrogen bond, so that the material can display strong activity. Those whose polarity is weak have weak activity, the catalytic activity is weak too. The results of chemical titration and XPS characterization show that the oxygen in the anhydride and lactone structures on the surface of carbonaceous materials are active oxygen, and which is the main active component, it can reduce the activation energy of methane dehydrogenation.

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1. Introduction

Many studies have been conducted in the field of producing synthesis gas from CO_2–CH_4 catalytic reforming in recent years [1–14]. The focus falls on the active components, carrier, assistant and carbon deposit as well as the thermodynamics and dynamics of the reforming reaction. Selection of catalysts for CO_2 reforming methane is paid to the precious metals and transition metals. Although the transition metal catalyst has better catalytic activity,

it has such defaults as serious carbon deposit, high temperature sintering and solid-phase reaction with the carrier, which reduces its activity and shortens its life. Advantages of precious metal catalyst, such as Rh, Ir, Pt and Pd, lie in that the lower reaction temperature, less energy consumption, but these metals are rare and cost more [3–5,15]. Therefore, it is a key for industrializing CO_2 reforming methane to develop an active and steady catalyst under mild condition with the least cost.

As catalyst, carbonaceous materials have the following advantages: cheap, acid and alkali resistant, having developed pore structure, large specific surface area and excellent adsorptive property. Thanks to these advantages, carbon catalysts are becoming the target for studies and one kind of the most potential catalysts in realizing the industrialization of CO_2 reforming

Table 1
Ultimate and pore analysis of carbonaceous materials.

Carbonaceous materials	Ultimate analysis (%, ad)					Ash (%, ad)	SSA (m^2/g)	PSV (cm^3/g)	d_p (μm)
	C	H	O	N	S				
CC-carbon	89.87	0.27	0.75	0.86	0.36	7.80	85.65	0.06	19.82
DT-carbon	88.30	1.40	2.50	0.92	0.50	6.41	93.80	0.08	12.40

CC, Taiyuan Coal Coke; DT, Datong.

methane [16–27]. However, relevant reports on CO_2–CH_4 reforming over carbonaceous material catalysts are not so many. To deepen understanding of the catalysis nature of carbonaceous material in CO_2–CH_4 reforming, the influence of different conditions on carbonaceous material catalytic CO_2–CH_4 reforming is studied by using a fixed-bed reactor. The surface structure and functional groups of carbonaceous material have been characterized through SEM, XPS, XRD and chemical titration before and after the reaction.

2. Experimental

2.1. Catalytic activity measurements

Experiments were carried out in a continuous-flow quartz reactor (I.D. 20 mm) packed with particle size of 125 meshes, 100 mg catalyst. After heating for a given setpoint, CH_4/CO_2 mixture (CH_4/CO_2 = 1) was introduced into the reactor [28–31]. The gas hourly space velocity (GHSV) was 2000 h^{-1}. After reaching steady-state conditions, the gases were periodically analysed by a gas chromatography. Prior to analysis, the effluent was passed through a water-trap at 0 °C in order to remove reaction water. CH_4 and CO_2 conversion was calculated as followed:

$$X_{CH_4} = \frac{F_{CH_4\ in} \times Y_{CH_4\ in} - F_{CH_4\ out} \times Y_{CH_4\ out}}{F_{CH_4\ in} \times Y_{CH_4\ in}} \times 100\%$$

$$X_{CO_2} = \frac{F_{CO_2\ in} \times Y_{CO_2\ in} - F_{CO_2\ out} \times Y_{CO_2\ out}}{F_{CO_2\ in} \times Y_{CO_2\ in}} \times 100\%$$

where X is the CH_4 or CO_2 conversion; F is the gas flow rate of in and out, ml min^{-1}; Y is the different fraction volume percentage; Superscript in is the inlet; superscript out is the outlet.

2.2. Preparation of carbonaceous materials

Two different carbonaceous materials were used in the experiment. The materials were prepared by pyrolysis of coal at 1150 °C for 1.5 h, then crushed to 30–200 mesh-size particles. The composition, the specific surface area and pore specific volumes of carbonaceous materials are provided in Table 1. The mineral matter analyses in carbonaceous catalyst ash were performed with a VARIAN atomic absorption spectrophotometer. Result was shown in Table 2. Previous studies have found that the ash contained in the carbon material has little effect on reforming reaction conversion (effect can be ignored) [4]. Therefore, the effect the ash on reforming conversion does not consider in this study.

Table 2
Analysis result of mineral matter in carbonaceous catalyst.

Element	CaO	MgO	Fe_2O_3	Na_2O	K_2O
Mass fraction (%)	0.71	0.42	0.89	0.34	0.45

2.3. Characterization

The crystalline structures of the catalysts were observed by XRD with a Dandong DX-2700 apparatus, equipped with a monochromator for the Cu-K_α radiation (Cu-K_α, λ = 0.154 nm), operating at 40 kV and 30 mA. Spectra were scanned in the range from 10° to 80°. Scanning speed was 8°/min under atmospheric pressure.

Morphology of the catalyst sample was determined by JSM-6700F type scanning electron microscope, resolution was 1.0 nm. The catalyst samples were deposited on thin amorphous carbon films supported by copper grids.

XPS analyses were performed with a V.G. Scientific ESCALAB250 using focused monochromated Al-K_α ($h\nu$ = 1486.6 eV, 150 W).

The BET specific surface area of the catalysts was analyzed with a Sorptmantic 1990 instrument using nitrogen as adsorbed at 77 K.

3. Results and discussion

3.1. Carbon catalytic CO_2 reforming of methane

3.1.1. Effects of carbonaceous material on the conversions of CH_4 and CO_2

Fig. 1 shows the influence of temperature on methane pyrolysis and CH_4–CO_2 co-conversion under non-catalytic condition. From the figure, it can be seen that the trend of methane pyrolysis and CH_4–CO_2 co-conversion is the same. With the increase of reaction temperature, methane conversion of CH_4–CO_2 co-conversion is a little higher than that methane pyrolysis. Besides, the conversion of methane is obviously higher than that of CO_2 under the condition of mixed CH_4–CO_2 gases. Under the non-catalytic condition, several reactions may happen as follows:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \tag{1}$$
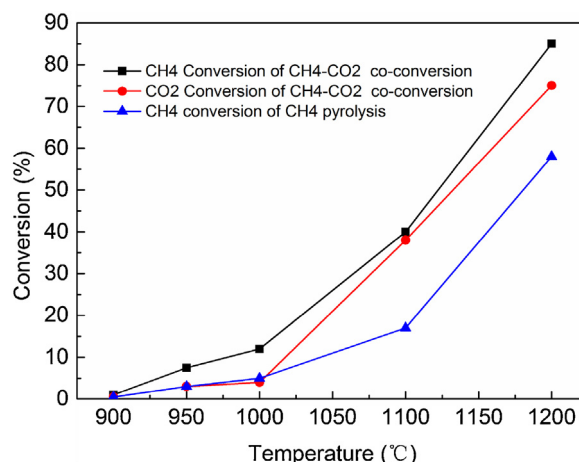
$$C + CO_2 \rightleftharpoons 2CO \tag{2}$$

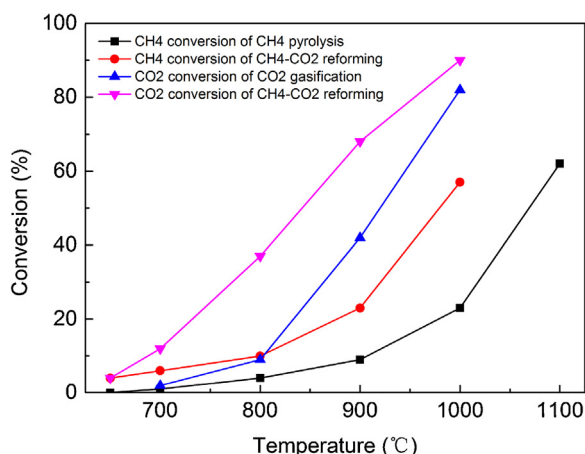**Fig. 1.** Conversion vs temperature in different feed gas without catalyst.

Fig. 2. Conversion vs temperature in different feed gas over DT-carbon catalyst.
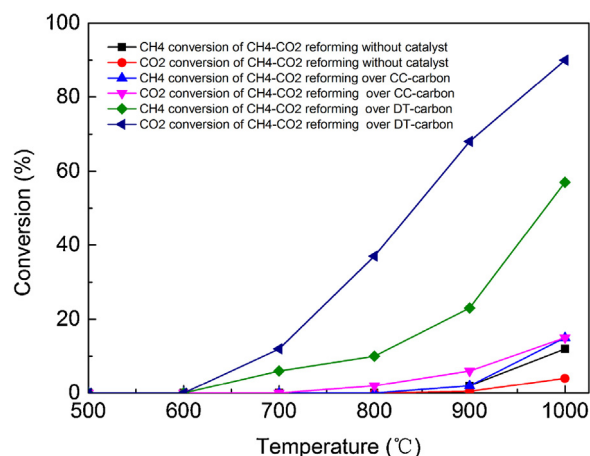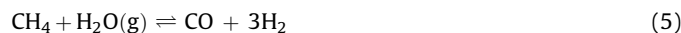

Fig. 3. Conversion vs temperature in different carbonaceous materials.

$$CH_4 \rightleftharpoons C + 2H_2 \tag{3}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O(g) \tag{4}$$

$$CH_4 + H_2O(g) \rightleftharpoons CO + 3H_2 \tag{5}$$

There is no liquid water found during the reaction. It means under non-catalytic condition, the CH_4–CO_2 reforming, water–gas shift and steam reforming reaction seldom or do not happen. However, the obvious carbon deposit forming has been found after CH_4–CO_2 co-conversion without catalyst. It means methane pyrolysis has happened during the process, and the pyrolysis rate of methane is higher than the gasification rate of CO_2. The conversion of methane in pyrolysis and CH_4–CO_2 co-conversion is almost the same. It means that the probability of CH_4–CO_2 reforming is very small under non-catalyst condition. The main reason why the methane conversion of CH_4–CO_2 co-conversion is a little higher than that of methane pyrolysis lies in the gasification reaction due to the existence of CO_2, which breaks the balance of reaction.

Fig. 2 shows the influence of temperature on methane pyrolysis, CO_2 gasification and CH_4–CO_2 co-conversion over carbonaceous materials. It can be known that the conversion of methane in CH_4–CO_2 co-conversion is obviously higher than the pyrolysis of methane. It means the existence of carbonaceous material can promote CH_4–CO_2 reforming reaction. Meanwhile, it is found that CO_2 conversion of CH_4–CO_2 co-conversion is remarkably higher than that of CO_2 gasification, which further proves that CH_4–CO_2 reforming has happened over carbonaceous material. Comparison between Figs. 1 and 2 reveals that methane conversion of CH_4–CO_2 co-conversion and methane pyrolysis has been noticeably improved over carbonaceous material. That means carbonaceous material plays the role of catalyst in methane pyrolysis and CH_4–CO_2 reforming.

3.1.2. Effects of different carbonaceous material on conversions of CH_4 and CO_2

Carbon material is a kind of porous carbonaceous material. Different carbonaceous materials have distinct features. The property of the catalyst is closely related to the kind and physicochemical property of carbonaceous materials. Two carbonaceous materials have been selected to study the influences of different carbonaceous material on the reforming reaction. Results are shown in Fig. 3. It can be seen that DT carbonaceous materials have more catalytic activity, while CC carbonaceous material has

no obvious catalytic activity on the reforming reaction. That may be due to the fact that compared with CC carbonaceous material, DT carbonaceous material has a larger specific surface area and developed pore structure (Table 1), so its ability of absorbing and dissociating CH_4 and CO_2 has been improved. It exhibits high catalytic activity. Li et al. [28] also has proven that the carbonaceous material owning larger specific surface area and low ash content has higher catalytic activity. Besides, factors influencing the feature of carbonaceous material are quite complicated [28,29], such factors as the kind of coal, ash content and kind and the reaction condition in treatment all have a certain effect on the feature.

It also can be seen from Fig. 3, the influence of reaction temperature on the conversion of CH_4 and CO_2 is in the same trend: with the increase of reaction temperature, their conversion will increase. When the temperature increases to 900 °C from 700 °C, the conversion of CH_4 and CO_2 increase from 6% and 12% to 23% and 68%, respectively. The main reason is that the reforming reaction is an endothermic reaction. So, it has a positive influence on the reaction with an increase in temperature. According to thermodynamic calculation, the temperature of CH_4–CO_2 reforming is above 640 °C. As can be seen from the graph, there is an almost linear increase in conversion of CH_4 and CO_2 over carbon material after 650 °C. It shows that the reaction temperature has a more powerful influence on CH_4–CO_2 reforming. However, the increase in reaction temperature needs more energy consumption. So, the conversion of feed gas can be improved through prolonging the gas–solid contact time at the proper temperature.

3.1.3. Effects of CH_4 partial pressure on the conversions of CH_4 and CO_2

CH_4–CO_2 reforming is a reaction where volume can be increased. The partial pressure of methane has significant influence on the conversion of reaction gas and the volume fraction of H_2 and CO in syngas. Fig. 4 shows the influence of different methane partial pressures on CH_4–CO_2 conversion at the temperature of 900 °C. From the figure, it can be seen that the conversion of methane and CO_2 is different under the different partial pressures of methane, but the overall trends are almost the same: conversion drops quickly to be steady with the increase of reaction time. The major reason lies in that firstly, at the beginning of reaction, there is no reforming product H_2 and CO in the reactor, which is good to the undergoing of reforming according to thermodynamic equilibrium; secondly, at the beginning of the reaction, there are many active sites on the surface of carbonaceous material. And 20 min later, conversion comes to a steady level. With the increase of partial pressure of methane, the conversion of
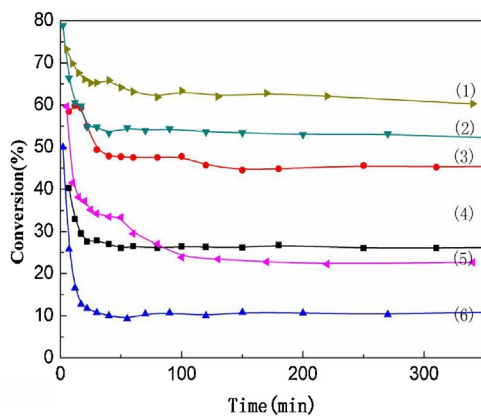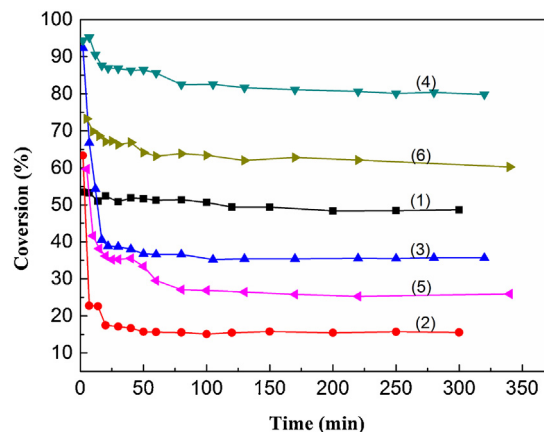
(1) X_{CO_2}, CH$_4$:CO$_2$=1:1;（2）X_{CO_2}, CH$_4$:CO$_2$ = 2:1;（3）X_{CO_2}, CH$_4$:CO$_2$ = 1:2
（4）X_{CH_4}, CH$_4$:CO$_2$=1: 2;（5）X_{CH_4}, CH$_4$:CO$_2$ = 1:1;（6）X_{CH_4}, CH$_4$:CO$_2$ = 2:1

Fig. 4. The conversion at different CH$_4$/CO$_2$ ratio.

(1) Conversion of CO$_2$ at 0.36 L/(g.h); (2) Conversion of CH$_4$ at 0.36 L/(g.h)
(3) Conversion of CH$_4$ at 0.09 L/(g.h); (4) Conversion of CO$_2$ at 0.09 L/(g.h)
(5) Conversion of CH$_4$ at 0.18 L/(g.h); (6) Conversion of CO$_2$ at 0.18 L/(g.h)

Fig. 5. Conversion of CH$_4$ or CO$_2$ at different airspeed.

methane is decreasing and it comes to the lowest when CH$_4$/CO is 2. That is mainly due to: on one hand, the carbon deposit from methane pyrolysis of excess methane reduces the catalytic activity of carbonaceous material; and on the other hand, the increase of partial pressure makes the content of the methane increase in the reaction system, thus the relative conversion of methane reduces though the overall dynamic drive become stronger. When CH$_4$/CO$_2$ is 0.5, the conversion of methane hits the peak, but its increase is not obvious compared with CH$_4$/CO$_2$ being 1. To the contrary, an excess of CO$_2$ reduces its relative conversion. On the whole, the proportion of CO$_2$ can be increased to a proper level in order to improve the methane conversion in reforming process.

3.1.4. Effects of airspeed on the conversions of CH$_4$ and CO$_2$

In the process of gas–gas or gas–solid reaction, the reactant should firstly go through the gas film on the outer surface of catalyst particle to contact with the surface of the catalyst. Generally speaking, the diffusion resistance of gas film can be ignored when the gas flow speed excesses to a certain value. Therefore, the influence of change in gas flow speed on reaction speed can help to remove the influence of external diffusion and facilitate the dynamics study on the reaction. Fig. 5 shows the influence of gas flow speed on the conversion of CH$_4$ and CO$_2$ when the gas flow speed increases from 90 ml/(g h) to 360 ml/(g h) at the temperature of 900 °C. It can be seen from the figure that lower gas flow speed, higher conversion of CH$_4$ and CO$_2$, which means the influence of external diffusion has less influence on the reaction within a certain scope. When the gas flow speed is 360 ml/(g h), the conversion of CH$_4$ and CO$_2$ is 15% and 50%, respectively. When the flow speed is 180 ml/(g h), the conversions are 25% and 65%, respectively. When the speed drops to 90 ml/(g h), the conversion increases to 38% and 85%, respectively. The main reason is that due to the decrease of gas flow speed, CH$_4$ and CO$_2$ can have a longer time to contact with the carbonaceous material, so residence time can be prolonged. The increase of residence time makes the feed gas fully absorbed and diffused, thus the conversion of CH$_4$ and CO$_2$ can be improved. Studies have shown that thanks to the influence of water gas shift reaction, the conversion of CO$_2$ is higher about 11% than that of CH$_4$ in dry reforming. However, Fig. 5 shows that the gap between CO$_2$ and CH$_4$ conversion can reach to 35 over carbonaceous material, and it becomes larger with the decrease of gas and solid contact time. Therefore, it can be inferred that a few carbonaceous materials have been gasified by CO$_2$.

3.1.5. Compositions of synthesis gas

In industrial application, the compositions of synthesis gas have an important influence on subsequent products. Therefore, it is of great significance to study the composition of synthesis gas from CO$_2$–CH$_4$ reforming over carbonaceous material. Table 3 shows the influence of different reaction temperatures on the composition of synthesis gas. It can be seen that the effective components in the product gas (CO + H$_2$) increase gradually and H$_2$/CO decreases with the increase of reaction temperature. When the reaction temperature is 800 °C, the effective content of the synthesis gas is 41%. When the temperature is 900 °C, the effective content increases to 69%. When the temperature reaches to 1000 °C, the effective content increases to 92%. Meanwhile, when the temperature increases to 900 °C from 800 °C, H$_2$/CO drops to 0.7 from 0.8. Afterwards, with the temperature continues to rise, H$_2$/CO does not change obviously. The major reason lies in that the gasification reaction happens between CO$_2$ and carbonaceous material at high temperatures. With higher temperature, the gasification becomes quicker. It makes the content of CO more than H$_2$ in the synthesis gas. When the temperature is above 900 °C, H$_2$/CO stays unchanged. It means that CO$_2$–CH$_4$ reforming dominates gradually at high temperatures. Li et al. reported the same results [28].

3.2. Characterization

3.2.1. SEM

Different carbonaceous materials have similar changes shown in the SEM picture after the reaction. So the SEM picture of one material has been selected to characterize, which is shown in Fig. 6. From Fig. 6(a), it can be seen a great amount of irregular carbon substance similar to the fish-scale structure on the surface of the carbonaceous material before the reaction; this carbon substance may be the residue of some coal volatilizing in destructive

Table 3
Syngas distribution form CO$_2$–CH$_4$ reforming at different temperature.

Temperature (°C)	CO (%)	H$_2$ (%)	CO + H$_2$ (%)	H$_2$/CO
800	22.26	19.02	41.28	0.85
900	40.23	28.97	69.20	0.72
1000	53.76	38.27	92.03	0.71
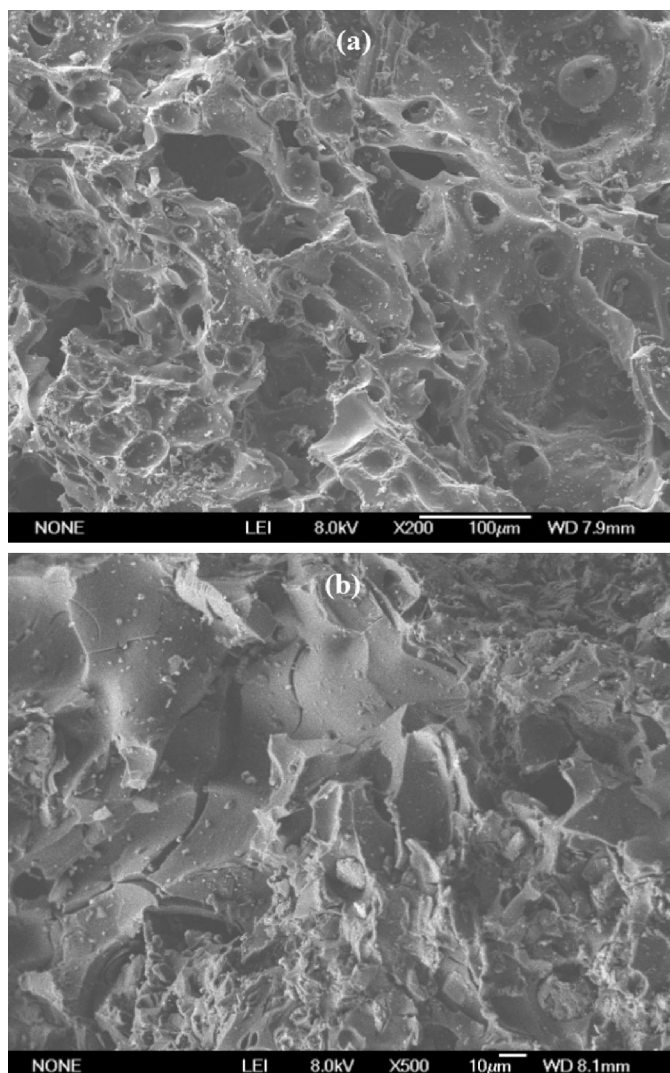
(a) Raw sample; (b) sample after reaction under 3.6MPa

Fig. 6. SEM of samples.

distillation. After the reforming reaction, the substance on the surface almost disappears and graphitization displays on the edge of pores, which means the reforming reaction is companied by the gasification reaction of carbon. Studies also reveal that the fish-scale substance has stronger catalytic activity and gasification activity as well as consumption [28]. At the beginning of the reforming reaction, the conversion of CH_4 and CO_2 is very high. There are two major reasons: the first one is fish-scale substance on the original carbonaceous material is an active catalyst in CH_4–CO_2 reforming; the second one is that with larger specific surface area and abundant pore structure, the original carbon has stronger ability of absorption and dissociation at the beginning. It can facilitate the absorption and diffusion of CH_4 and CO_2, and make these gases have a full contact with the active substance of catalyst [30,31]. With the reaction going, the conversion decreases gradually to a steady level. That is because with the prolonging of reaction time, the active fish-scale carbon on the edge will be consumed gradually, and the carbonaceous material itself will appear (Fig. 6(b)). The activity and the gasification reactivity of carbonaceous material are lower than those of the fish-scale carbon, but it is more stable. With the increase of reaction time and reaction temperature, carbon deposit from methane pyrolysis can cover the surface of carbonaceous material gradually to block the

small-pore structure in the reforming. While the small pores make great contribution to the specific surface area of catalyst, thus the activity of catalyst will be reduced or inactivated on one hand. On the other hand, the carbonaceous material itself will be graphitized gradually on the other hand. Due to the lower activity of graphitization, the conversion is reduced.

3.2.2. Specific surface area and pore volume

Heterogeneous catalytic reaction usually happens on the surface of catalyst particles. So the size of carbon material's specific surface area and pore structure distribution can influence the performance of catalyst and the absorption ability of reactant gases directly. In order to have a more in-depth understanding the reforming reaction, the specific surface areas of carbonaceous material before and after the reaction under different conditions has been measured, which is shown in Table 4. From the table, it can be seen that the specific surface area and pore volume of carbonaceous material after methane pyrolysis and reforming reaction are significantly reduced. The major reason is that the carbon deposit produced deposits on the surface and small pores of carbonaceous material. The smaller pores are the greatest contributor to the specific surface area, thus the specific surface area and pore volume of carbonaceous catalyst can be reduced [32]. Besides, some small pores of carbonaceous material can merge and disappear or close because of the different expansion coefficients of many substances inside the carbonaceous material at high temperatures when the reforming reaction can happen [33].

3.2.3. Oxygen functional groups

The variety and number of functional groups on the surface of carbonaceous material exert great influence on the chemical properties of carbonaceous material [34,35]. The most important group on the surface is the oxygen functional group. Shu et al. [36] think that the oxygen in the carbonaceous material includes the polar state and non-polar state such as the OH group, carboxyl group and the phenolic hydroxyl group whose polarity is strong. They can associate with H in methane molecules as the dipole force, and their activity is relatively stronger and is an active oxygen functional group. While the dipole effect of oxygen in the ether oxygen group is very weak, it is called inactive oxygen. However, there are still some problems in the study on the property of carbonaceous materials because of its complicated structure. In terms of its development, it requires more under-standings and studies on the nature of the functional groups inside the carbonaceous material, especially the study on the variety and content of oxygen functional groups. Oxygen functional groups on the surface of carbonaceous material have been characterized with the method combining physics and chemistry. Fig. 7 and Table 5 show the characterization results before and after the reaction, respectively. From Fig. 7 and Table 5, it can be seen that great changes have happened in the groups and the contents of the phenolic hydroxyl group, carboxyl group and lactonic group decrease obviously. Especially, the contents of the phenolic hydroxyl group and lactonic group in the carbon catalyst are 28.7% and 2.6% before the reaction, respectively. While at the temperature of 1000 °C, their contents decrease to 4.2% and 0.2% after reforming, respectively. That is in the CO_2–CH_4 reforming

Table 4
Specific surface area and pore volume.

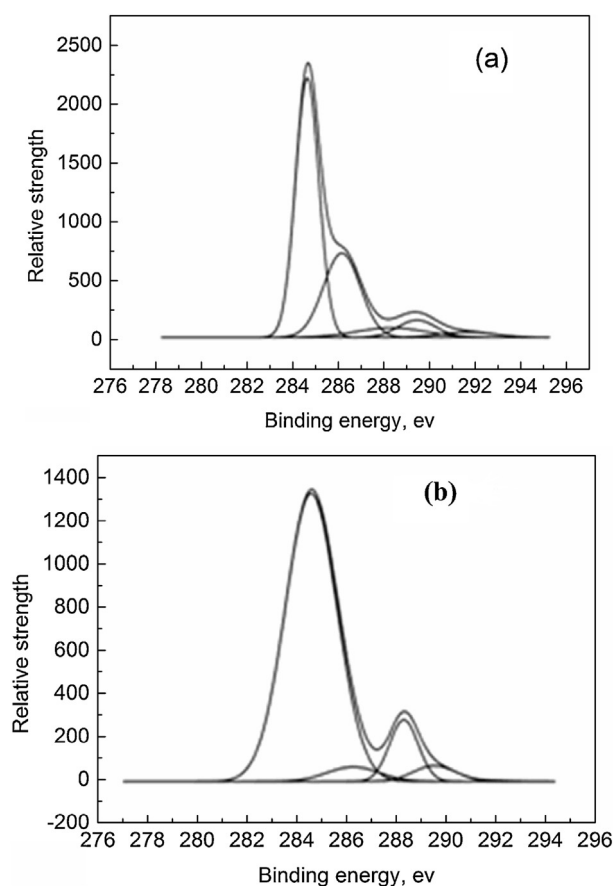|	Raw sample	Sample of after CH_4 pyrolysis at 750 °C	Sample of after CH_4–CO_2 reforming at 1000 °C	Sample of carbon deposition
BET (cm^2/g)	84.19	2.67	70.40	12.60
PV (cm^3/g)	0.05	0.01	0.01	0.05

Fig. 7. XPS of different samples.

over carbonaceous material, oxygen-containing on the surface of carbonaceous material is consumed obviously. What is more, from the discussion above, the catalytic activity of carbonaceous material drops noticeably after CO_2–CH_4 reforming. It can be inferred that the phenolic hydroxyl group and lactone have an important impact on the reforming reaction, which can promote the conversion of methane [29–31,37,38]. However, since the phenolic hydroxyl group and lactonic group are expendable substance, they will be consumed with the going of reaction. And after they have been consumed up, the activity of the catalyst will drop and stay at a new stable value.

Table 6 is the result of chemical titration about oxygen functional group on the surface of carbonaceous material before and after the reaction. XPS comparison reveals that the changing trend of oxygen functional group by chemical titration is in line with the characterization result from XPS: the content of the oxygen-containing functional group decreases obviously after reforming. The contents of the carboxyl group, lactonic group, phenolic hydroxyl group and the carbonyl group drop from 0.0071, 0.0147, 0.0097 and 0.0116 before the reaction to 0.0035, 0.0072, 0.0053 and 0.0054 after reforming, respectively. From Table 6, it can be seen that after the reforming, the contents of oxygen

Table 5
The change of oxygen-bearing functional group in carbonaceous material.

Item	The content of oxygen-bearing functional group (%)				
	C–C	Phenolic hydroxyl	Carbonyl	Carboxyl	Lactone
Before reaction	56.6	28.7	6.1	6.1	2.6
After reaction	82.2	4.2	9.8	3.7	0.2

Table 6
Boehm titration results ($mmol\,g^{-1}$).

	Carboxyl group	Lactone group	Phenolic hydroxyl group	Carbonyl group
Raw sample	0.0071	0.0147	0.0097	0.0116
Sample after reforming	0.0035	0.0072	0.0053	0.0054

functional groups on the surface of carbonaceous material (except carbonyl group) all decrease. That demonstrates that the oxygen in groups with acid and lactone structure is active oxygen and is the major active substance of carbonaceous material. These active substances can reduce the activation energy of methane de-hydrogenation. The activity of catalyst depends on the polarity of oxygen in oxygen species. Various oxygen species make the nature of electrical energy on the surface of oxygen in oxygen species different. Polar oxygen can be used as dipole force to associate with H bond of methane to demonstrate the strong activity of carbonaceous material. The first condition of reforming reaction is the activation of methane, which is a process of chain reaction. Chain initiation is the key in methane activation. It is that methane can be activated by the active sites on the surface of carbonaceous material. At the beginning, the polarity of oxygen in oxygen functional groups – carboxyl group, lactonic group and phenolic hydroxyl group is so strong, and it can associate with H in methane molecular in the form of H bond to reduce the activation energy of methane de-hydrogenation, thus the reforming reaction can be boosted.

And then with the going of reaction, the polar oxygen is consumed up gradually, leaving non-polar one whose dipole force is too weak, so the catalytic activity of carbonaceous material will decrease.

3.2.4. XRD

Fig. 8 shows the X-ray diffraction analysis on a carbonaceous material sample before and after the reaction. This figure reveals that the location of peak before and after the reaction changes obviously. Attribution analysis on the diffraction peak of minerals has been conducted with the reference to the book of Map Manual of Thermal Analysis, Powder Crystal Analysis and Phase Change of Minerals [39]. The analysis reveals that calcite and quartz are the major components of the original carbonaceous material sample. After the reaction, quartz has no any change while $CaCO_3$ disappears, which means during the process of reaction, the ash
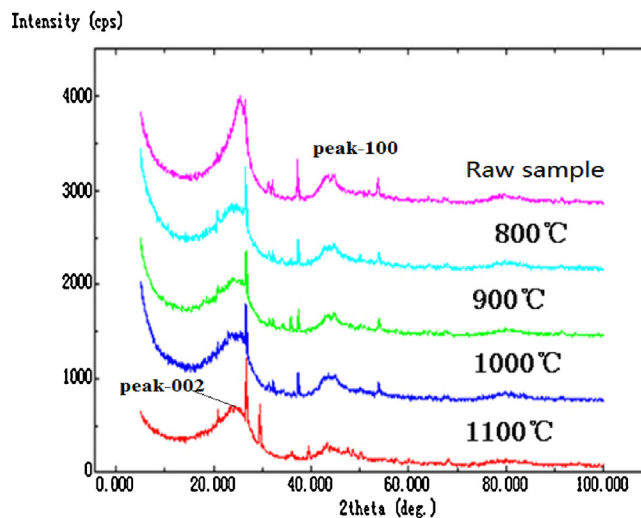

Fig. 8. XRD patterns.

in the carbonaceous material can also affect the reforming reaction. In addition, this figure shows that the intensity of two microcrystalline peaks – 0 0 2 (parallel orientation of the aromatic plane) and 1 0 0 (the size of the aromatic plane) all decrease. Especially, at the temperature of 1100 °C, the peak of 1 0 0 disappears after the reaction. It indicates that the carbonaceous material's ordered structure becomes not so well-structured in the process of reforming reaction which may result from the gasification of CO_2.

4. Conclusions

In conclusion, this study has shown that the carbonaceous material plays the role of catalyst in CH_4–CO_2 reforming. While with carbonaceous material, CO_2 gasification, methane pyrolysis and CO_2–CH_4 reforming can take place at the same time, with the reforming as the main reaction, CO_2 gasification and methane pyrolysis as the side reaction. Catalytic activity varies from one carbonaceous material to another, but their reaction trend is the same on the whole. Those high specific surface area carbonaceous materials show higher catalytic activity. The increase in reaction temperature and residence time of the reforming can improve the conversion of reactant gas. Adjusting the partial pressure of methane can control the carbon–hydrogen ratio of the synthesis gas. XPS and XRD studies demonstrate that the structural ordering of carbonaceous materials becomes a little messier after the reforming reaction, and the number and content of oxygen functional groups decrease. That means these oxygen functional groups on the surface of carbonaceous materials are involved in the reforming and these groups along with pore structure on the surface are the major factors influencing the catalytic properties. Different oxygen species make the nature of electrical energy on the surface different; the catalytic activity depends on the polarity of oxygen from different species. Those whose polarity is strong have strong activity, which can be associated with methane in the form of hydrogen bond. Those whose polarity is weak have weak activity.

Acknowledgements

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