

Research Article

Research of Hydrogen Preparation with Catalytic Steam-Carbon Reaction Driven by Photo-Thermochemistry Process

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An experiment of hydrogen preparation from steam-carbon reaction catalyzed by K_2CO_3 was carried out at $700^\circ C$, which was driven by the solar reaction system simulated with Xenon lamp. It can be found that the rate of reaction with catalyst is 10 times more than that without catalyst. However, for the catalytic reaction, there is no obvious change for the rate of hydrogen generation with catalyst content range from 10% to 20%. Besides, the conversion efficiency of solar energy to chemical energy is more than 13.1% over that by photovoltaic-electrolysis route. An analysis to the mechanism of catalytic steam-carbon reaction with K_2CO_3 is given, and an explanation to the nonbalanced $[H_2]/[CO + 2CO_2]$ is presented, which is a phenomenon usually observed in experiment.

1. Introduction

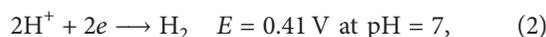
Hydrogen is an important energy material to fuel cell and various chemicals such as methanol, dimethyl ether, and synthetic gasoline. The traditional way to obtain hydrogen is to decompose the methane and water, which consumes a lot of other powers such as electricity. Therefore, the technical improvements to make hydrogen generation a cost-effective reality have become challenging subjects.

The sunlight is an inexhaustible and cost-free source of energy. The direct use of solar energy to obtain hydrogen is the most desirable way that has drawn wide attention from energy scientists all over the world [1–4]. There were three ways in the past decades to produce hydrogen by solar energy: photovoltaic-electrolysis (PVE), photo-electrochemistry (PEC), and photo-thermochemistry (PTC). PVE makes use of solar cell to drive electrolysis of water, which is a way to directly convert solar energy into chemical energy [5]. Since the water electrolysis has been a mature technology, PVE process is maturer than the other two solar-to-hydrogen processes currently. The PEC makes use of electrochemical reactions [6–8] driven by quantum effects of photoirradiation on semiconductor metal oxide (SMO) catalytic anode which is connected to an external circuit. On

the base of optical excitation, the excited electrons on SMO are removed from the anode to cathode through external circuit. The four holes were left in the catalytic anode of SMO, where the water can be split as follows.



At cathode the H^+ is reduced:



where E is the reduction potential. The production of hydrogen by PTC uses concentrated solar radiation as the energy source to drive cycle redox reaction at more than 1500 K [9–11], such as the pyrogenation of $ZnO \xrightarrow{\text{solar}} Zn + (1/2)O_2$ and the oxidation of $Zn + H_2O \rightarrow H_2 + ZnO$ by turn.

The energy conversion efficiency (ECE) of solar-to-hydrogen is defined as [6]

$$\eta_{\text{solar-fuel}} = \frac{\Delta H}{Q_{\text{solar}}}, \quad (3)$$

where Q_{solar} is the solar energy input (in kJ) and ΔH is the high heating value (HHV) of the fuel produced. The ECE of solar-to-hydrogen by PVE is about 10%, which is

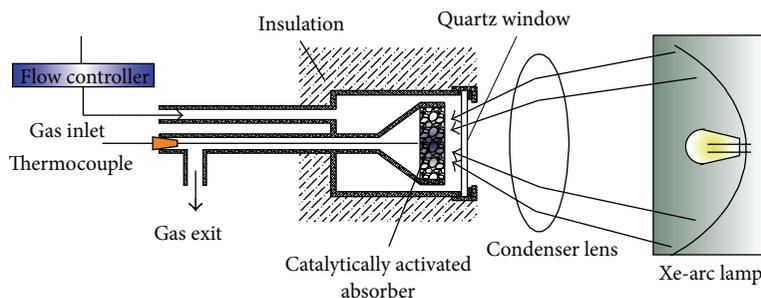


FIGURE 1: Schematic of the main part in experiment.

determined by the efficiencies of solar-to-electricity (17%) and the water electrolysis (60%). For photo-electrochemistry, the ECE is determined by the photon energy level in which the electron in catalytic anode is pumped from a donor to an acceptor. The quantum effects to excite electron result in a poor utilization of the solar spectrum and low solar energy conversion efficiency (less than 2%). In conclusion, the hydrogen production from solar thermochemical cycles is the most desirable path, but the products Zn(g) and O₂ must be quickly quenched at high temperature to avoid their recombination, which inevitably bring the heat loss and result in ECE lower than 10% in experimental operations.

In fact, there are more simple ways to produce hydrogen by solar energy, for example, the endothermic reactions of



These reactions can be achieved at temperature about 700°C by catalyst, which is more easily carried out with concentrated solar reactor. Wörner and Tamme [12], Kodama et al. [13], and Berman et al. [14] had achieved many encouraging progresses in the carbon dioxide reforming of methane driven by concentrated solar. They had obtained the solar-hydrogen ECE of 45% on MW levels of solar concentrator with efficiency of solar to heat by 85%.

In this study, the hydrogen was prepared by catalytic steam-carbon reaction at 700°C, which was driven by a concentrated solar reactor. The generation rate of hydrogen has been investigated with different contents of potassium carbonate. A special attention was paid to the impact of catalyst content and the reaction mechanism onto the energy conversion efficiency over the process.

2. Experimental

2.1. Preparation of Feedstock. The feedstock was prepared with equivalent-volume impregnation method. The pre-weighed potassium carbonate was dissolved with deionized water to obtain the impregnation solution; then the pre-weighed granular activated carbon with the size of 20~40 meshes (0.38 mm~0.83 mm) was then impregnated in the configured solution for four hours. After that, it was transpired by water bath at 80°C and then dried at 110°C for

more than ten hours to thoroughly remove the moisture. A series of feedstock was prepared with potassium carbonate contents of 0%, 10%, 15%, and 20% in weight. The phase and morphology of the typical feedstock were characterized by X-ray diffraction (XRD, Dandong, China, Cu/Kα radiation, voltage: 40 kV, current: 25 mA; scanning rate: 2°/min; scan range: 2θ = 30°~80°) and transmission electron microscopy (Tecnai G2 F20 S-TWIN, USA, voltage: 200 KV).

2.2. Experimental Arrangement. Figure 1 shows the main part of the experimental facility; it consists of the simulated solar concentrator and the reactor. The reactor included a tundish-like reaction bed in diameter of 40 mm, where the feedstock was filled. Temperature in reaction bed was monitored by a thermocouple. The solar concentrator was simulated by focusing Xe-lamp irradiation. The facular diameter at reaction bed was about 3 cm. The energy flux onto the reaction bed was measured by LJ-II laser power meter (Chinese testing technology research institution). Changing the input power of Xenon lamp could adjust the value of energy flux. The typical average energy flux of 120.1 KW/m² could be obtained with the Xenon lamp powered 1000 W, at which the reaction bed temperature was about 700°C for experiments.

Figure 2 is the flow chart of the experiment. After argon of 60 mL/min purged the air in reaction bed filled with feedstock, heating the temperature of reactor to 700°C. Then the micropump was turned on, and the water was fed into steam generator. The steam carried by argon of 60 mL/min was fed into reaction bed, where the steam-carbon reaction took place. The exiting gases through washing, condensation, and drying were then analyzed by gas chromatograph (GC7900, using TDX-01 packed column 3 mm × 2 mm and TCD detector). The gas flow was measured by a bubo soap-film flowmeter.

Each experiment with different potassium carbonate was carried out at the same conditions: temperature of 700°C, water rate of 0.27 mL/min, feedstock of 1.2 g, and reaction time of 45 minutes.

2.3. Data Treatment. The main reaction of steam with active carbon is



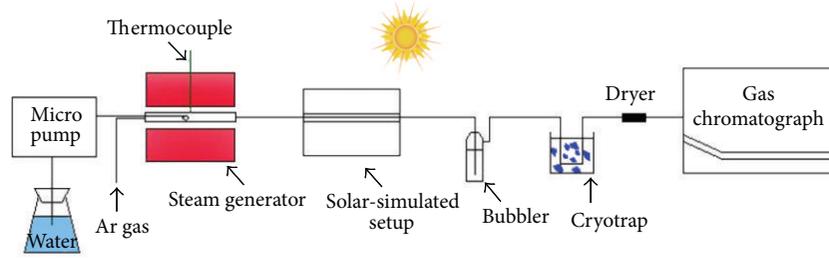
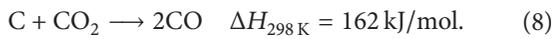


FIGURE 2: Experimental flow diagram.

and the incidental reactions are



The conversion rate of carbon was defined as

$$X(\text{C}) = \frac{(N_{\text{CO}} + N_{\text{CO}_2})}{N_{\text{C.in}}} \times 100\%, \quad (9)$$

where N_{CO} and N_{CO_2} are the releasing cumulants (in moles) of CO and CO₂ with reaction process, respectively, and the $N_{\text{C.in}}$ is the primary moles of activated carbon. To estimate the efficiency of optical energy served in chemical energy, according to reference [6], the energy conversion efficiency of the present process is redefined as

$$\eta = \frac{\sum H_{\text{out}}^i - \sum H_{\text{in}}^i}{\rho \cdot S \cdot t}, \quad (10)$$

where $H_{\text{out}}^i, H_{\text{in}}^i$ are the high heating values (HHVs) of the fuel produced and exhausted in reaction process, respectively; ρ the average energy flux at catalysis bed; S the facular area; t , the reaction time.

3. Results and Discussion

3.1. Performance of Steam-Carbon Reactions with Different Catalyst Contents. In order to evaluate the catalytic performance of potassium carbonate in steam-carbon reaction, the experiments with different catalyst contents of 0, 10%, 15%, and 20% were carried out; the results are shown in Figure 3.

It can be found that there is an obvious difference between noncatalytic steam-carbon reaction and catalytic reaction. In the initial stage, the generation rate of hydrogen and carbon monoxide is about ten times to that without potassium carbonate, but there is less difference among that with potassium carbonate contents of 10%, 15%, and 20%. Similar results were also found in steam gasification of coal char catalyzed with K₂CO₃ by Wang et al. [15], where, at catalyst loading lower than 7.5%, the gasification was slow even with prolonged gasification time. Both observations are in agreement with that the catalyst is activated in steam-carbon reaction only when the initial potassium carbonate loading is larger than a threshold value, above which the catalytic activity is obvious, but less difference in its content

larger than 10% [16]. The changes of generation rates with time can be explained by the model of core shrinkage. In the initial stage of reaction, the surface of solid reactant is bigger than that in the later stage because of the carbon exhausted. There are more molecular contacts between steam and carbon, which leads to more reactions.

By Figures 3(b) and 3(c), though the generation rate of CO₂ takes on the trend of initial increase and then decrease, the ratio of CO₂/CO increases throughout the reaction process. This can be understood with the competition between (7) and (8). It can be conjectured that (7) is a gaseous volume reaction, in which the reaction possibility is constant; while (8) is a surface reaction on carbon, its reaction possibility is impacted by the surface of solid reactant. In the initial stage, there is more carbon existent; it makes reaction (8) consume CO₂ and the reaction possibility of (8) become less and less in the later stage of reaction because of the carbon exhausted.

It is worth noticing the ratio of [H₂]/[CO + 2CO₂] from experimental results. Assuming that all H₂ is generated via reactions (6) and (7), the ratio would be equal to 1. The actual ratio estimated in Figure 3 is somewhat greater than 1 in the initial 20 minutes, only in the middle stage is matching in the estimation, and then below the estimation in the last stage. However, the average [H₂]/[CO + 2CO₂] ratios are close to the estimation as reported by [15]. The reason for this observation will be discussed in Section 3.3.

Figures 4(a) and 4(b) show the carbon conversion and hydrogen yield calculated by cumulant with time over the reaction process, respectively. Figure 4(c) is the energy conversion efficiency calculated by (10). At the initial stage, the ECE is 27.6%. With time passing, the carbon exhausted and the reaction rate decreased, the ECE reached and 13.1% in the end of experiments. However, it is still larger than 10.89% by photovoltaic-electrolysis method.

3.2. TEM and XRD Analysis of Reactants. The TEM and XRD results were shown in Figures 5 and 6, respectively. The dark part in Figure 5 is regarded as K₂CO₃ crystalloid, which was randomly distributed in or on the active carbon clusters. Because the active carbon is amorphous, only the characteristic diffraction of K₂CO₃ can be detected with the samples before and after reactions. It proves the K₂CO₃ acts as a catalyst in experiments.

3.3. Mechanism of Steam-Carbon Reaction Catalytic by K₂CO₃. Moulijn and Kapteijn [17] have presented a theory

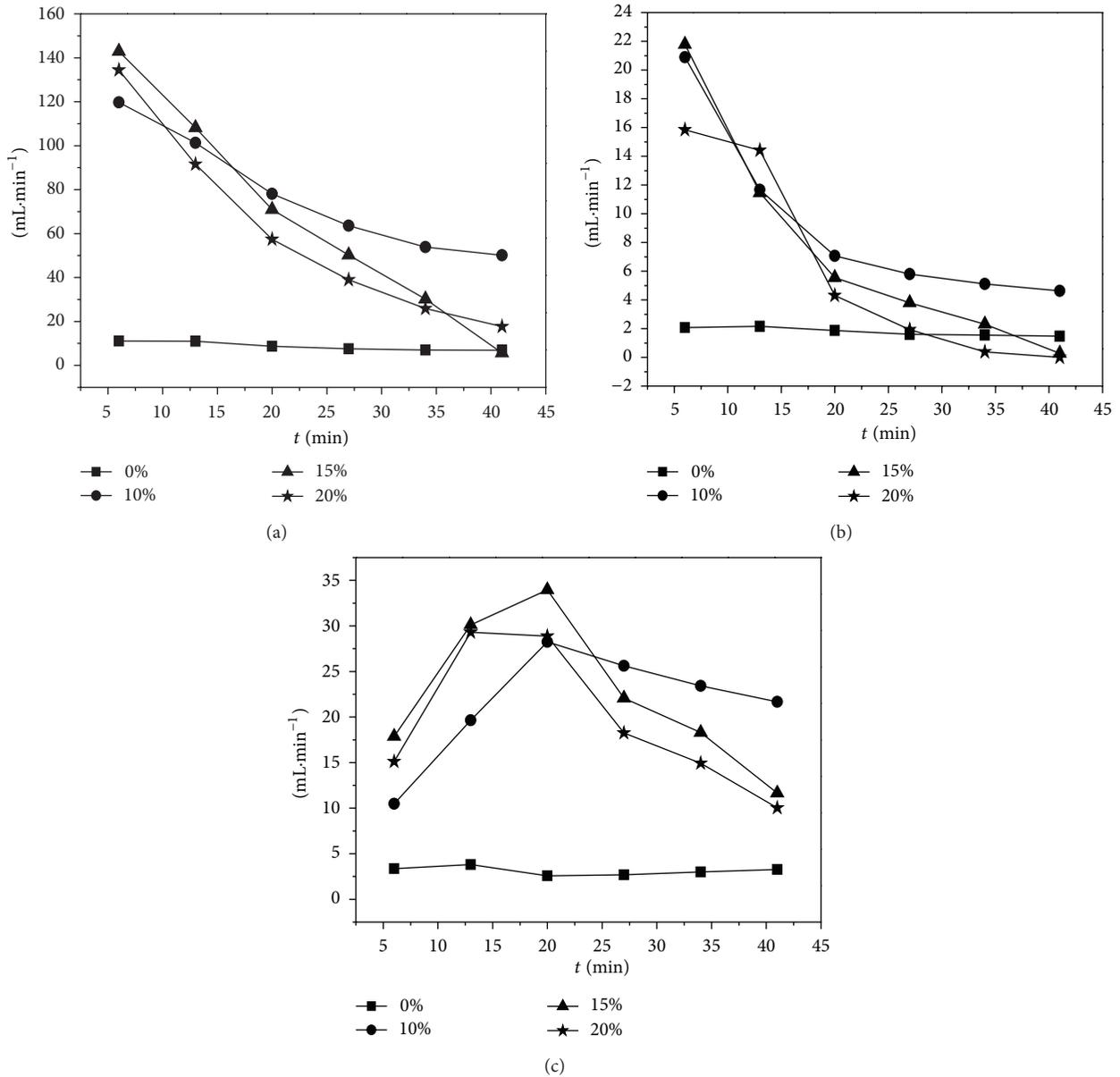
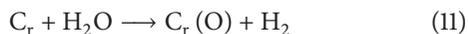


FIGURE 3: The generation rate versus time in experiments with different catalyst contents. (a) Hydrogen, (b) carbon monoxide, and (c) carbon dioxide.

to describe the mechanism of noncatalytic gasification of carbon. They considered that there were some chemically active sites formed by the lacunas or unsaturated carbon chains on carbon surface, which had ability to adsorb oxygenic atoms. In the steam-carbon reaction, the H₂O molecular was adsorbed by those active sites to form C_r(O) intermediates and release H₂. Then the C_r(O) intermediates ran away from solid carbon by their thermal motion at high temperature, and a newborn site was left. The process can be expressed as follows:



The calculation of quantum mechanics by Wjgmans et al. [18] should told that there would be formed C–O–M clusters when alkali metals oxides (AMO) were soaked on carbon surface by the function of AMO attracted electron. The valence electron of carbon atom close to AMO would tend to AMO and then result in those carbons with positive electricity to trap chemically oxygenated chemicals to form C_r(O) intermediates.

Considering from the above, the catalytic reaction of steam-carbon by K₂CO₃ can be conjectured. During the reactor bed at 700°C, the K₂CO₃ firstly decomposed into K₂O and CO₂; K₂O then functioned according to the route shown in Figure 7 when steam was added in.

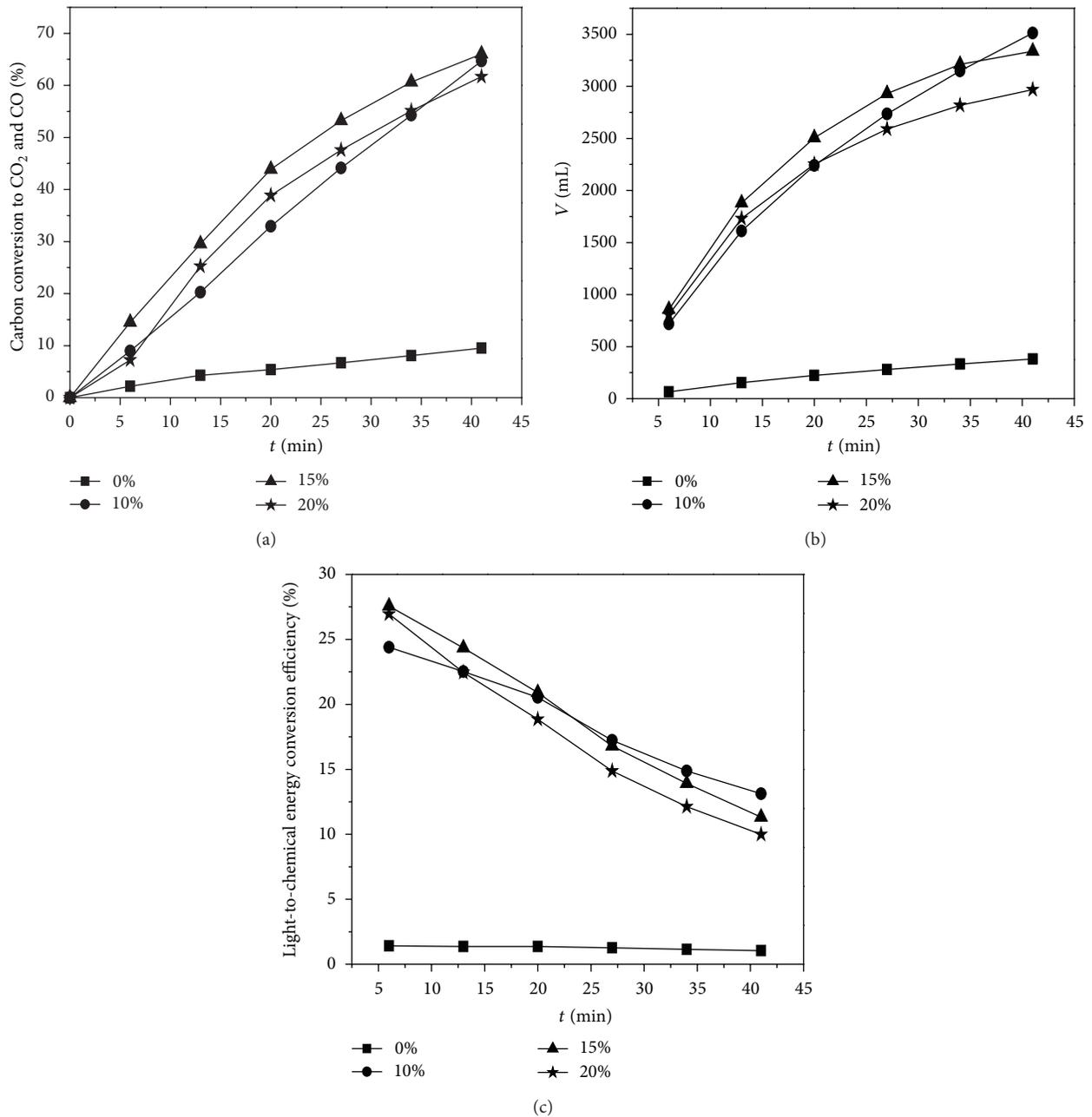
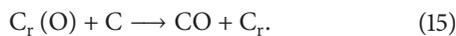
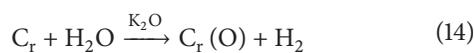
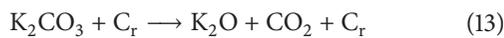


FIGURE 4: (a) Carbon conversion; (b) hydrogen production; (c) energy conversion efficiency during reaction.

Therefore, the catalytic process can be expressed as follows:



By this way, the catalytic effects of K₂O on steam-carbon reaction could be concluded in two aspects: one is to provide the amount of active sites on carbon surface; another is to decrease the activated energy to form C_r(O) intermediates.

The steam-carbon gasification is a heterogeneous catalytic reaction. It involves the adsorption, diffusion, reaction, and desorption on gas-solid surface. In the initial stage, the bigger precursor surface can provide many active sites. It makes chemical adsorption for H₂O molecular at these sites to release oxygen atoms and H₂. The C_r(O) intermediates were formed by these oxygen atoms and left from surface by their thermal motion. If the reaction temperature is not high enough, the C_r(O) intermediates could not leave in time. Therefore, the ratio of [H₂]/[CO + 2CO₂] is larger than 1 in the initial stage. When the C_r(O) intermediates reached saturation on carbon surface, the ratio is less than

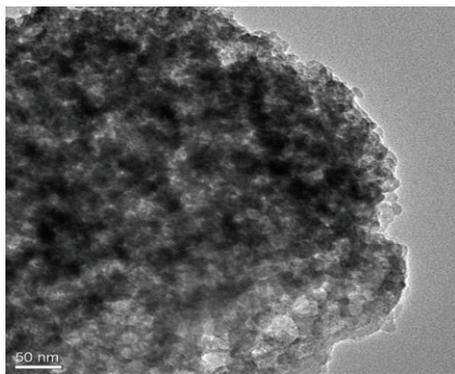
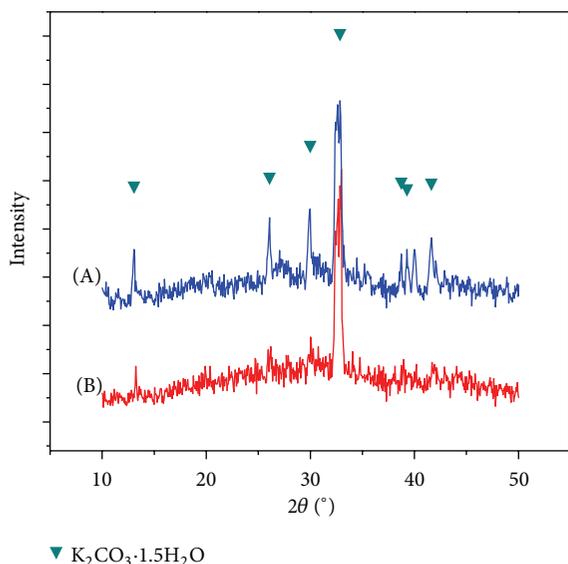
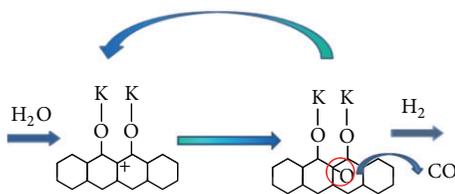


FIGURE 5: TEM images of feedstock.

FIGURE 6: XRD patterns of the feedstock with K_2CO_3 of 10%: (a) before reaction; (b) after reaction.FIGURE 7: H_2O-C catalytic reaction schematic diagram.

1 in the latter stage. This can be the reason why the $C_r(O)$ intermediates run away from surface in the controlling step of steam-carbon reaction, which was observed in many experiments.

4. Conclusions

The hydrogen preparation experiment was carried out with catalytic steam-carbon reaction driven by simulated solar energy, and the observations in experiments were analyzed.

There is something that can be concluded: with the K_2CO_3 catalyst, the reaction is achieved at temperature of $700^\circ C$, and the conversion efficiency of optical energy to chemical energy is more than 13.1% over that by photovoltaic-electrolysis route. The catalytic mechanism of steam-carbon reaction with K_2CO_3 was that the K_2CO_3 firstly decomposed into K_2O at higher temperature; then the K_2O-C^+ clusters were formed by the charge center displacement which was caused by electron interaction between K_2O and neighboring C atom. The H_2O was chemically adsorbed at K_2O-C^+ sites to form $C_r(O)$ intermediates and released H_2 at the same time, and the $C_r(O)$ intermediates were broken loose from carbon chain by their thermal motion; then a newborn site was left. This cycle repeated itself until the end of reaction.

Acknowledgments

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