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Experimental Study on a New Process of Producing Hydrogen in Consumption of Water and Coal

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A new process of producing pure H_2 in consumption of H_2O and carbon is presented. It contains three reactions: (1) Steam reacts with FeO at 800°C generating pure H_2 and Fe_3O_4/Fe_2O_3; (2) Fe_3O_4/Fe_2O_3 are reduced to FeO by CO at same temperature while CO changes to CO_2; (3) The produced CO_2 reacts with carbon generating CO at 900°C. The net product of the process is H_2 and CO. Theoretical energy gain of the new process is much higher than 1.0 and is energetically more than autarky. Some CO satisfies the process energy requirement and the surplus CO outputs as by-product. Experiments proved the feasibility of the process with indication of the importance to control the extent of reduction. The prominent advantages embedded allow the process applied in large-scale to trade coal for hydrogen. As such, instead of burning coal, hydrogen is burnt wherever energy is consumed. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 1388–1395, 2008

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Introduction

Coal is a major energy source of the world, especially in developing countries. For example, more than 70% of the total energy consumption is supplied by coal in China.[1] It is well known that burning coal causes serious environmental problems; therefore, miscellaneous clean coal technologies are proposed or being studied.[2] However, any fuel containing carbon element must generate CO_2 in combustion and leads to accumulation of CO_2 in the atmosphere. Therefore, a strategy of trading coal for hydrogen is presently studied. In the proposed strategy, hydrogen comes from water, but coal provides an inevitable chemical, carbon, to assist the production of hydrogen. If the strategy really becomes an energy policy, then it is not a dream that instead of burning coal, hydrogen is burnt wherever energy is consumed. There would not be CO_2 emission at all on consuming energy.

The most common technology of producing commercial bulk hydrogen as well as the hydrogen used for the synthesis of ammonia is steam reforming of natural gas, sometimes referred to as steam methane reforming (SMR).[3,4] At high temperatures (700–1100°C) and in the presence of a metal-based catalyst (Ni), steam reacts with methane to yield carbon monoxide and hydrogen.

$$CH_4 + H_2O = 3H_2 + CO \tag{1}$$

Additional hydrogen can be recovered by a lower-temperature gas-shift reaction with the carbon monoxide produced. The reaction is summarized to:

$$CO + H_2O = CO_2 + H_2 \tag{2}$$

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The general reaction is obtained by summing up Reactions 1 and 2:

$$CH_4 + 2H_2O = 4H_2 + CO_2 \tag{3}$$

Pure hydrogen cannot be directly obtained in the process, and the accumulation of carbon on catalyst is still an annoying problem. To simplify the separation of hydrogen, absorption of CO_2 with a metal oxide at the reaction temperature is proposed.[5] Practical high-temperature absorbent of CO_2 has, however, not been found. In addition, a huge amount of natural gas is consumed in producing hydrogen. Nine million tons of hydrogen was produced per year in the United States, mostly with the steam reforming of natural gas. The worldwide ammonia production, using hydrogen derived from steam reforming, was 109 million metric tones in 2004.[4] Natural gas is itself a clean fuel. It should be more applied as transportation fuel because better environment and less pressure on petroleum requirement could be expected.

Many thermochemical cycles of splitting water were reported in litrature.[6] However, the total energy efficiency of a H_2-production cycle will not be high if oxygen is produced at the same time since additional energy cost is paid to change the valence state of oxygen. A process of producing clean fuels should pass through a check of "theoretical energy gain." Theoretical energy gain (TEG) is defined as the ratio of theoretically releasable energy by the products over the theoretically invested energy in order to acquire the products. This conception is just like the weight ratio of cereals cropped in autumn to that of germs seeded in spring. Farming could not be sustained if the ratio is less than unity.

$$\begin{tikzcd}
T >> 25^{o}C & A \arrow[r, phantom, "+"] & B \arrow[r, phantom, "\overset{\Delta H_r^{\,T}}{=}"] & C \arrow[r, phantom, "+"] & D \arrow[d, "\Delta H_2"] \\
25^{o}C & A \arrow[u, "\Delta H_1"] \arrow[r, phantom, "+"] & B \arrow[r, phantom, "\overset{\Delta H_r^{\,25}}{=}"] & C \arrow[r, phantom, "+"] & D
\end{tikzcd}$$

Table 1. Standard Molar Formation Enthalpy of Substances at 298.15 K

Substances	C	H_2	Fe	CO	CO_2	H_2O	CH_4
ΔH_f kJ/mol	0	0	0	−110.54	−393.51	−285.83	−74.85

To illustrate the calculation of TEG, a general reaction shown below is taken for an example. The reaction occurs at a temperature, T, which may be much higher than the ambient temperature, for example, 25°C. ΔH_r^{25} and ΔH_r^{T} are the enthalpy changes of the reaction at 25°C and the reaction temperature, T, respectively. ΔH_1 is the enthalpy change of heating the reactants from ambient to the reaction temperature, and ΔH_2 is the enthalpy change of cooling the reaction products down to the ambient temperature. Since ΔH is a state function of thermodynamics, its value is determined only by the initial and final states, but not by the process connecting the two states. Therefore, theoretically $\Delta H_r^{25} = \Delta H_1 + \Delta H_r^{T} + \Delta H_2$. An assumption is embedded in the argument that ΔH_2 joined the energy balance because a comparison could not be made between different reactions otherwise. The value of ΔH_2 is affected by the value of T, which affects the thermal efficiency of an energetic process. ΔH_r^{25} is simply calculated from the formation enthalpies of materials involved in the reaction as that listed in Table 1.[7] TEG of the SMR process can thus be evaluated. The total enthalpy change of the SMR process at 25°C is $(-393.51)-(-285.83 \times 2-74.85) = 253$ kJ. The plus sign means that an energy input into the system is required in order to obtain the 4 moles of hydrogen. The reaction to release energy of the products is:

$$4H_2 + 2O_2 = 4H_2O \tag{4}$$

The enthalpy change of Reaction 4 is $-285.83 \times 4 = -1143.32$ kJ. The minus sign means energy output; therefore, the theoretically releasable energy on burning the products of Reaction 3 is 1143.32 kJ. The TEG of the process is $1143.32/253 = 4.52$. The TEG of water electrolysis is 1.0 since the reaction of consuming hydrogen is right the reciprocal of that of producing hydrogen. However, if the energy gain is less than unity, nowhere to find energy supply for the process in a long run. Practical energy gain is certainly much less than theoretical, therefore, a process that cannot pass the TEG examination is certainly of no practical value.

The proposed process is closely related to steam reforming but consumes different fossil fuel. A cycle of redox reactions of iron oxides is used to directly acquire pure hydrogen. The carbonized coal is used to produce a reductant necessary to maintain the cycle. However, contact of coal with water is purposely avoided. Coal must be carbonized before being applied in the process. Instead of carbonization in coking furnaces, coal is better be carbonized by supercritical extraction not only because of environmental concern, but also because more volatile compounds can be obtained and used for the preparation of transportation fuels.[8] Theoretical calculation and experiments will show the feasibility of the new process.

Fundamentals of new process

The proposed process of trading coal for hydrogen includes three reactions:

Reaction 1: Oxidation of FeO by steam at about 800°C. The product is pure hydrogen and Fe_3O_4/Fe_2O_3.

$$H_2O + 3\,FeO = H_2 + Fe_3O_4 \tag{5}$$

or

$$H_2O + 2\,FeO = H_2 + Fe_2O_3 \tag{5a}$$

Reaction 2: Carbon monoxide and hydrogen are the most common reducing agents of iron oxides used in commercial processes[9]; therefore, CO is used to reduce Fe_3O_4/Fe_2O_3 at the same temperature. The product is FeO and CO_2.

$$Fe_3O_4 + CO = 3\,FeO + CO_2 \tag{6}$$

or

$$Fe_2O_3 + CO = 2\,FeO + CO_2 \tag{6a}$$

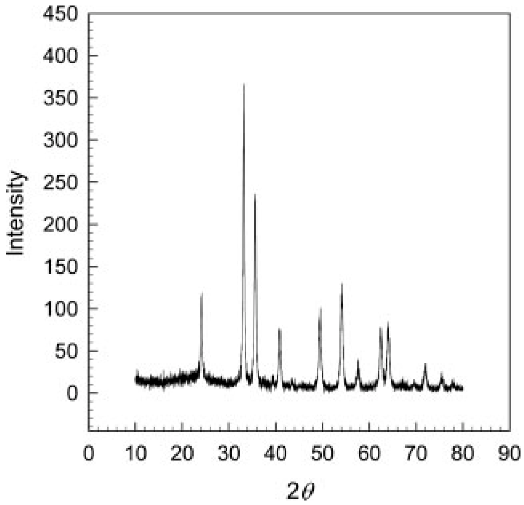

Figure 1. Wide angle XRD spectrum of SBA-15 loading iron oxide.

Reaction 3: The above produced CO_2 reacts with carbon at about 900°C generating the CO required in Reaction 2.

$$C + CO_2 = 2CO \tag{7}$$

Summing up reactions (5–7), a general reaction is obtained:

$$H_2O + C = H_2 + CO \tag{8}$$

Based on the general reaction, the energetic property of the process can be theoretically estimated. The energy input of the process is: $(-110.54)-(-285.83) = 175.29$ kJ. The theoretically releasable energy of the products is determined from the combustion reactions:

$$H_2 + 1/2O_2 = H_2O \tag{9}$$

$$CO + 1/2O_2 = CO_2 \tag{10}$$

The enthalpy change of Reactions 9 and 10 is -285.83 and -282.97 $(-393.51+110.54)$ kJ, respectively. The energy gain is, therefore, $(285.83+282.97)/175.29 = 3.24$. The new process of producing hydrogen is energetically less efficient than the SMR technology. However, the purpose of the present study is not to propose a more efficient process for hydrogen production, but to develop a technology of replacing the polluting fuel, coal, with a clean fuel, hydrogen. Although the TEG value is smaller than that of SMR process, it is considerably larger than that of water electrolysis. Theoretically, the process is energetically more than autarky. The energy input required by the whole process is 175.29 kJ, which is only 62% of that releasable by CO (282.97 kJ), one of the process products. Therefore, the other 38% of the produced CO can be output as a by-product. In addition, the new process bears some engineering merits. For example, steam never reacts with carbon, and H_2 and CO is generated in separate reactors. Therefore, pure H_2 is obtained without the need of subsequent separation/purification. While catalyst is very important for steam reforming technology, there is not a need for catalyst in the new process. Iron oxides play an important role in the process, but do not function as catalyst nor be consumed.

Should coal be carbonized and hydrogen be produced in situ at mining, long distance transportation of coal would be avoided. Instead, a hydrogen-fueled power plant can be built and electricity is transferred to remote. As a consequence, a lot of savings in energy cost and benefit to environment would be expectable.

Experimental

Several adsorbents were tested as the support of iron oxides, and the synthesized mesoporous silica material SBA-15 described previously,[10] the market available 13X zeolite and diatomite seemed to be promising among them. $Fe(NO_3)_3$ was loaded on adsorbent by a soaking method. The adsorbent loading $Fe(NO_3)_3$ was dried first at 60°C and then pressed into pellets. After drying at 120°C for 1 h, the pellets experienced different treatments. The SBA-15 pellets were heated in nitrogen atmosphere at 600°C for 3 h. The zeolite and diatomite pellets were sequentially heated at 200°C for 2 h, at 500°C for 2 h, and at 800°C for 3 h. The pellets were then crushed and sieved to get samples of particulate size 0.3 mm. The adsorbents are inert to the oxidation and reduction reactions of iron oxides, and they are not the catalyst either, therefore, the adsorbent loading iron oxides is named as process media (PM). The PM sample was examined with wide angle XRD. A spectrum obtained with the PM/SBA-15 sample is shown in Figure 1. The wide-angle XRD spectrum of SBA-15 does not show any remarkable peaks before loading iron oxide; therefore, the intensive refraction peaks of the spectrum belong to iron oxide.

The experiment using SBA-15 as the support of iron oxides and pure CO as the reducing gas is taken for an example to explain the experimental procedure. The reactor used in experiments is a quartz tube with 25 mm o.d. and 3 mm of wall thickness. The reactor is set in a vertical electric oven, whose temperature is under control and the constant temperature zone is about 120 mm long. In the reaction zone, 4.28 g PM/SBA-15 sample (containing 0.04271 mol iron) was packed. A flowsheet containing at least three reactors as shown in Figure 2 is necessary for a continuous operation. However, the reaction of carbon with CO_2 has been extensively studied in the research of activated carbon, therefore, is taken out of attention of the present study. To sim-

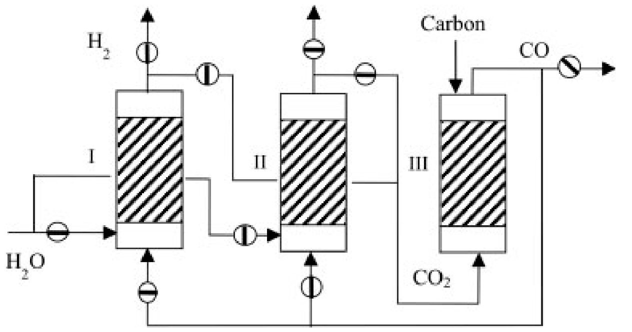

Figure 2. A schematic flowsheet for a continuous operation.

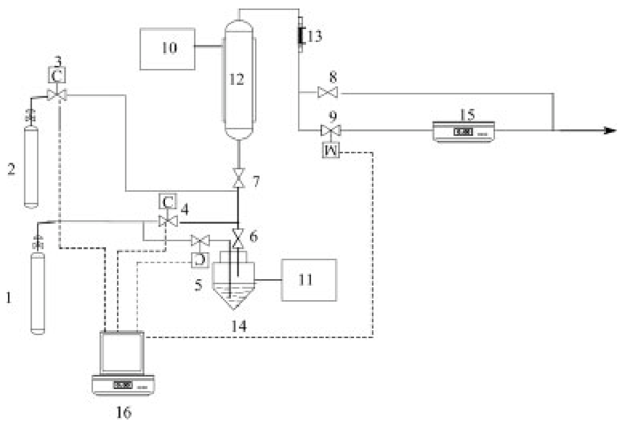

Figure 3. Experimental setup.

1: Ar cylinder; 2: CO cylinder; 3–5: mass flow controller; 6–8: solenoids; 9: mass flow meter; 10,11: temperature controller; 12: reactor; 13: condenser; 14: steam generator; 15: mass-spectrograph; 16: computer.

plify the experimental operation, a cylinder containing pure CO or its mixture with CO_2 is used for the supply of reducing gas. The actual experimental setup is shown schematically in Figure 3. Only one reactor was used to observe the transformation of iron oxides between the lower and higher valances. Argon was used as the carrier gas of steam, though a carrier gas is not necessary for large-scale production. Argon bubbled through a water bottle, whose temperature was adjustable and maintained constant. Both CO and argon used in experiments had purity higher than 99.95%. The gas flow rates were measured and controlled by mass flow controllers model SY9311 purchased from Beijing Sheng Ye Sci. & Tech. Develop Co. All signals of temperature and flow rates were sent to a computer, which processes and records the electronic signals and issues commands according to a prescribed program. A QMS Series Gas Analyzer purchased from Stanford Research was used to analyze the composition of effluent stream. The experimental procedure consists of four operations:

- *Reduction:* Carbon monoxide flows through mass flow controller 3 and solenoid 7 into the reactor and reacts with the iron oxide of higher valence. The effluent stream was analyzed in situ and then let out.
- *Sweeping:* The CO passage closes when the reduction reaction ends, and argon flows via mass flow controller 4 and solenoid 7 into the reactor to sweep the reaction gases out of the reactor and the massspectrograph.
- *Oxidation:* Argon flows into a steam generator through mass flow controller 5, bubbles in water and then flows out carrying steam through solenoids 6 and 7 into the reactor. The oxidation reaction occurs between steam and the iron oxide of lower valence. The effluent stream passes condenser 13 and analyzed.
- *Sweeping:* An argon stream is again used to sweep the reaction gases out of the reaction system.

Results and Discussion

The experimental results should logically be presented beginning with the production of hydrogen. However, the oxidation reactions that really occur depend on the result of reduction reaction, therefore, the latter was firstly presented.

Table 2. Dependence of Reduction Rate on Temperature

Series	Amount of PM (g)	Loading Ratio*	Fe in PM (g)	T (°C)	Reduction Time (min)
1	1.51	0.83	0.685	600	90
2	1.51	0.83	0.685	700	60
3	1.50	1.66	0.936	800	55
4	1.50	1.66	0.936	900	50

*Amount of Fe loaded per unit weight of SBA-15.

Reduction period

Effect of Temperature. The reaction rate of reduction is remarkably slower than that of oxidation; therefore, the effect of temperature was tested at first in order to find out an appropriate temperature with reaction rates compatible for both reactions. The test condition and the result are shown in Table 2. Clearly, the reaction rate increases following the increasing temperature. Although more load of iron oxide allows for longer time of reduction, the time needed at 800 and 900°C is considerably less than that at 600°C and 700°C, though the loading ratio of iron oxide is doubled. However, to balance the effect of temperature on reduction and oxidation, relatively lower temperature is preferred. In addition, the reaction rate increases not considerably from 800 to 900°C; therefore, 800°C was selected in the present study.

Identification of Three Reduction Stages. The temperature of reactor was kept unchanged when reduction succeeds oxidation. CO flowed into the reactor at a rate of 74.94 cm^3/min after sweeping the reactor with an argon stream. The composition of the effluent stream during the reduction period is shown in Figure 4. Because the reactor was initially full of argon, the reduction started 500 s later since CO

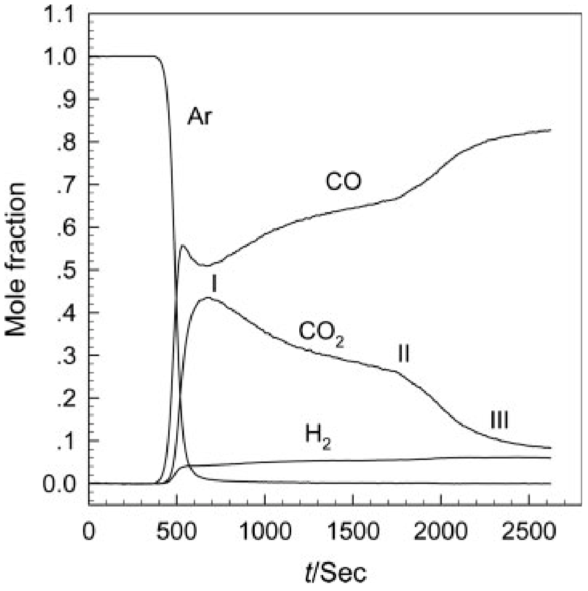

Figure 4. Composition of the effluent stream during reduction period.

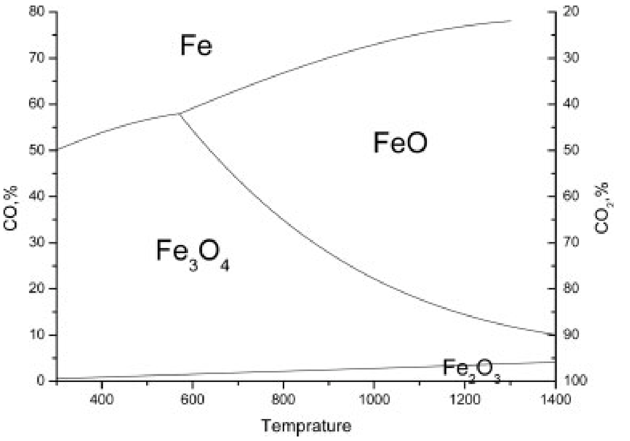

Figure 5. Phase diagram in reducing ferric oxides with CO.

entered. The concentration of Ar in the effluent stream decreased drastically following the increase of CO and CO_2 concentration. However, CO_2 concentration decreased again after reaching a maximum, and the decreasing rate became faster at about 1750 s, and slowed down again at about 2500 s. As such, the CO_2 concentration curve separates the reduction period into three stages as marked with Roman numbers. The three stages indeed correspond to different reduction reactions as is subsequently discussed. Hydrogen was also observed in the effluent stream and made up 5% of the effluent. The hydrogen appeared in the reduction period might come from the residual water of previous phase or the water contained in the support. However, hydrogen did not appear if a mixture of CO and CO_2 replaced pure CO as reducing gas.

Effect of Reduction Extent. The product of the reduction reaction can be either metal iron or ferrous oxide depending on the reaction temperature and the composition of reaction atmosphere as shown in Figure 5.[11] Controlling the extent of reduction reaction is important for keeping the process stable. Because the reduction reaction is proceeding at the molecular/atomic level, the generated fresh iron, if it is the reduction product, must be dispersed over the support surface at atomic level. There is not a strong interaction between metal iron and the support surface as schematically shown in Figure 6; therefore, the very tiny iron solids must be blown out of the reaction zone by the effluent stream. However, should FeO be the reduction product, a stronger interaction between the Si—O and Fe—O bonds would be expected, and FeO has the same crystal structure as Fe_3O_4[12]; therefore, it will stay on the support surface.

Because the reactor was full of Ar before CO enters, the concentration of CO in the gas phase starts from zero, but increases quickly. It is argued, therefore, that the reduction products are consecutively Fe_3O_4, FeO, and Fe at 800°C according to the phase diagram shown in Figure 5. Thus, the aforementioned Stage I of the reduction reaction corresponds to the transformation of Fe_2O_3 to Fe_3O_4, and Stage II corresponds to the transformation of Fe_3O_4 to FeO. The reaction rate of the second transformation is slower than the first one; therefore, a maximum is formed on the composition curve as shown in Figure 4. Stage III corresponds to the transformation of FeO to metal Fe with an even slower reaction rate. It is possible to keep the reduction reaction stopped at the FeO stage by controlling the reaction temperature and CO concentration in the reaction atmosphere. Having FeO as the reduction product, the whole reduction process will also be maintained at a relatively faster speed.

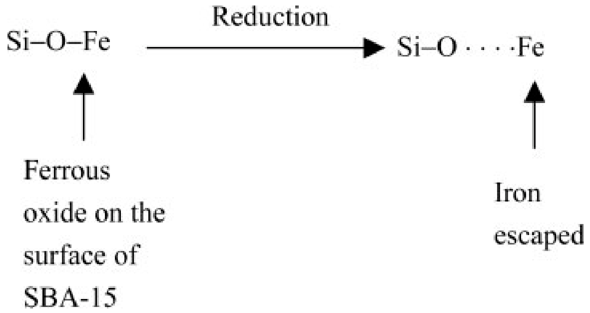

Figure 6. Different interactions between carrier surface and metal iron or iron oxide.

The argument on the reduction procedure is supported by a calculation of product quantity. The calculation is based on the constancy of gas flow rate at both the entrance and exit ends of the reactor. The gas volume will not change during the reduction period no matter with what iron oxide the reduction reaction starts. The recorded rate of the effluent stream shown in Figure 7 proved the constancy. Therefore, the recorded composition curves shown in Figure 4 can be used to calculate the component flow rate by timing it with a constant (flow rate of the effluent stream). The total amount of CO_2 generated in the reduction period is

$$N_{CO_2} = \int F_{CO_2}(t)\, dt \tag{11}$$

where $F_{CO_2}(t)$ is the flow rate of CO_2, which was obtained as the product of the total flow rate of effluent stream (a con-

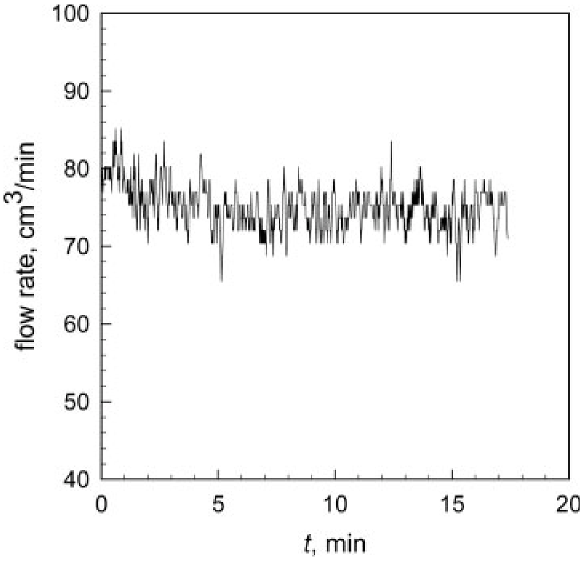

Figure 7. Recorded flow rate of effluent stream for the reduction period.

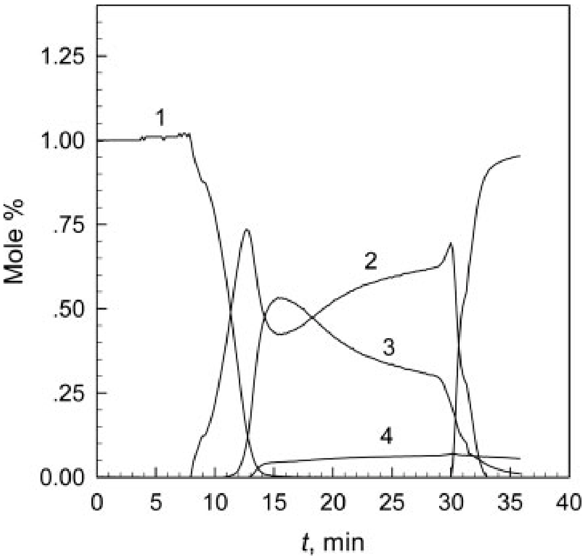

Figure 8. Composition curves of the effluent stream in the reduction period avoiding phase III.

1: Ar; 2: CO; 3: CO_2; 4: H_2.

stant) and the composition of CO_2 in the effluent stream, and a software Origin completed the calculation. Based on the partition of three stages for the reduction period, the quantity of CO_2 generated in each stage is calculated. The specific data used in the calculation are: Temperature = 800°C, amount of PM = 4.28 g containing 0.0427 mol of Fe, and the flow rate of reducing gas (CO) = 74.5 cm^3/min. The reaction occurring in the first stage, as previously mentioned, is

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \tag{12}$$

Theoretically, the moles of CO_2 generated are 1/6 of that of iron, i.e., 0.00712 mol. The calculated amount of CO_2 generated in the first stage is 0.00782 mol. The difference between the theoretical and the calculated values is only 10%, therefore, agreement between them is observed. The reaction occurring in the second stage is

$$Fe_3O_4 + CO = 3FeO + CO_2 \tag{13}$$

The theoretical amount generated in this stage is one third of iron, i.e., 0.01424 mol. The calculated amount generated in the second stage is 0.01518 mol. The difference between the theoretical and the calculated values is only 6.7%. Apparently, the theoretical and the calculated values are in agreement. Assumption of the three stage reduction is, therefore, quite reasonable, and the consecutive reduction reactions of ferric oxides were also indicated elsewhere.[12]

The reduction reaction in the third stage is the transformation of FeO to metal Fe, which is better to be avoided, and the reduction period should stop at the end of Stage II. Therefore, another run was consequently carried out. The reducing gas (CO) was switched to sweeping gas at the end of Stage II for the second run. The recorded composition of the effluent stream in this run is shown in Figure 8. Compared to Figure 4, the composition curve of CO_2 drops much faster. However, the Stage III reaction cannot be totally avoided because CO cannot disappear suddenly. The reaction in Stage III is

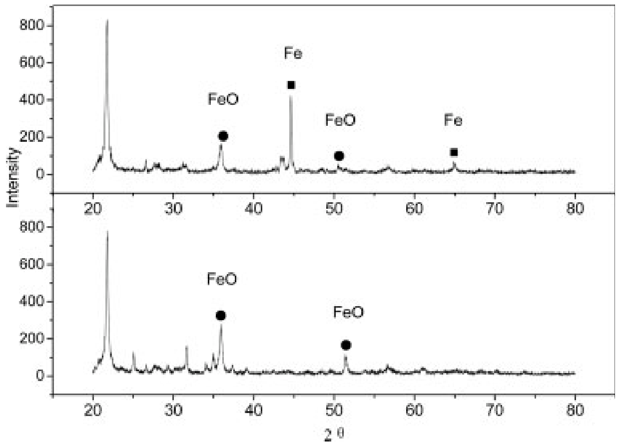

Figure 9. XRD spectrums of a diatomite sample loading Fe_2O_3 after reduction.

Top: reduced by pure CO; Bottom: reduced by a mixture of CO and CO_2.

$$FeO + CO = Fe + CO_2 \tag{14}$$

However, this reaction cannot proceed completely because the concentration of CO in the reaction atmosphere decreases fast, and the reaction will stop if the concentration of CO becomes lower than about 67% according to Figure 5. Therefore, the actual quantity of metal iron is much less than expected. As shown in Figure 9, complete avoidance of metal iron is possible if, instead of pure CO, a mixture of CO and CO_2 is used as reducing gas. The production rate of hydrogen will be stable in so doing as shown in Figure 10. Avoidance of forming metal iron avoids the formation of

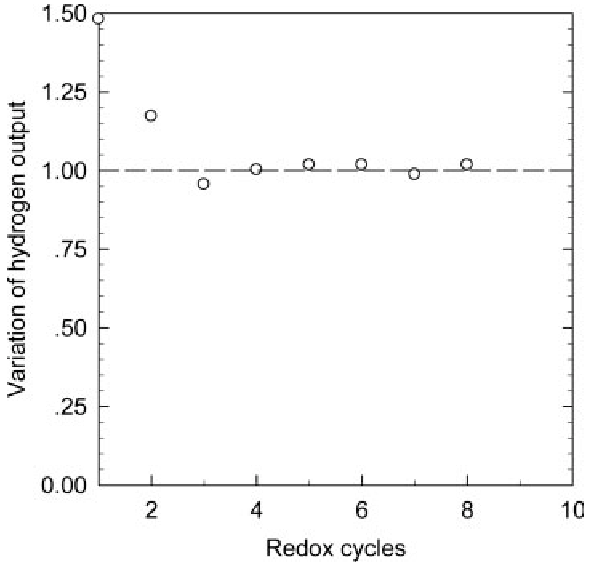

Figure 10. Stability of hydrogen production in consecutive reduction/oxidation cycles using a mixture of CO and CO_2 as reducing gas.

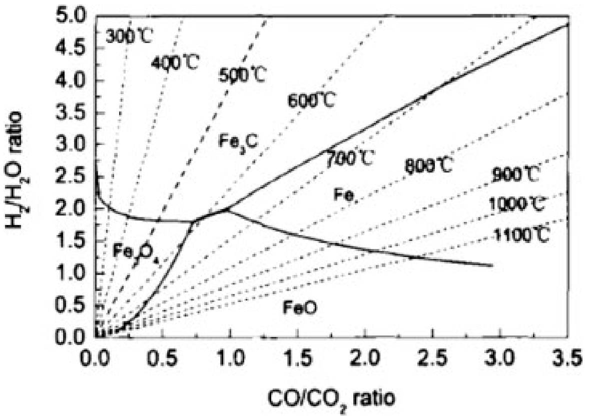

Figure 11. Effects of H_2/H_2O and CO/CO_2 ratios on Fe_3C formation.

iron carbide because metal iron is the prerequisite condition of forming iron carbide for temperatures higher than 628°C.[13] Iron carbide can hardly form at 800°C even H_2 joined the reducing gas as shown in Figure 11.[14]

Oxidation period

When the operation switched to oxidation period, steam reacted with FeO and pure hydrogen was obtained, meanwhile FeO was oxidized to an oxide of higher valence (Fe_3O_4 or Fe_2O_3). The temperature of the steam generator was kept at 95°C (The saturation pressure of water is 84.517 kPa), and the flow rate of the carrier gas was kept at 55.02 ml/min while the reaction zone was maintained at 800°C. The composition of the effluent stream reported by a mass spectrograph is shown in Figure 12. It is shown that the effluent stream contains only H_2 and Ar, and neither CO nor CO_2 was detected, therefore, pure hydrogen is produced in large-scale production. The gas flow rate at both ends of entrance and exit of the reactor is supposed to be same during the oxidation period no matter whether Fe_2O_3 or Fe_3O_4 is the oxidation product. However, the recorded flow rate of the effluent stream is not constant as shown in Figure 13. Existence of metal iron in the reducing products is responsible for the inconstant flow rate. As indicated in previous section, some metal iron might be produced in the third stage of reduction if pure CO was used as the reducing gas. The oxidation reaction of metal iron with steam is

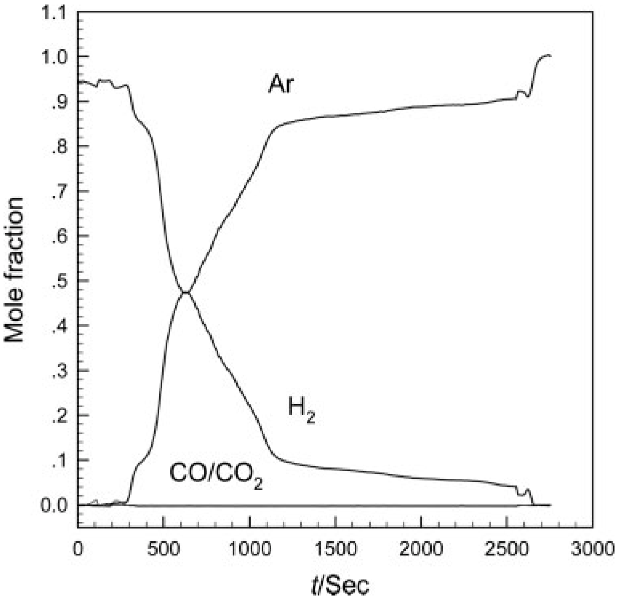

Figure 12. Composition of the effluent stream during oxidation period.

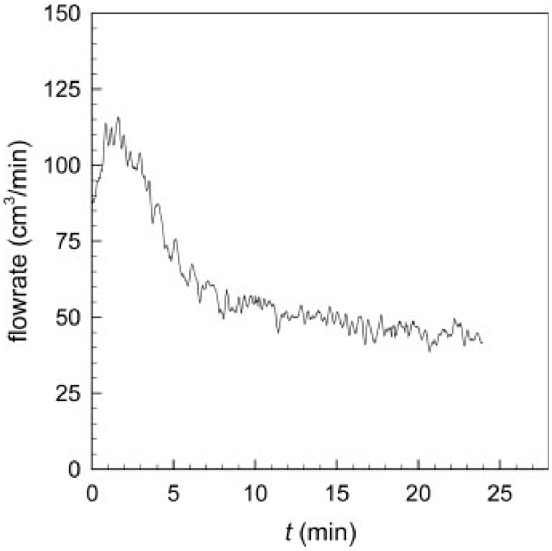

Figure 13. Flow rate of the effluent stream during oxidation period.

$$4H_2O + 3Fe = Fe_3O_4 + 4H_2 \qquad (15)$$

or

$$3H_2O + 2Fe = Fe_2O_3 + 3H_2 \qquad (15a)$$

Although only one mole H_2 produced in the reaction of steam with FeO (Reaction 5 or 5a), 3 or 4 moles H_2 produced in the reaction of steam with metal iron (Reaction 15 or 15a). In addition, metal iron is much more reactive than FeO with steam. Therefore, metal iron is initially consumed yielding an overshoot on the flow rate of the effluent stream, and the flow rate decreased following the exhaustion of metal iron.

Comparison with counterpart processes

A short discussion is given to compare the proposed process with counterpart ones. A water-splitting process basing on the Fe_3O_4/FeO cycle[15,16] releases oxygen at an elevated temperature to realize the cycle between iron oxides of different valences. Extra energy cost must be paid for keeping the reactor operations cycling between two temperatures, and the huge thermal capacity of real reactors renders the cycle a very slow process. The iron oxide of higher valence is reduced to FeO in terms of CO presently. Therefore, cycling the redox reactions of iron oxides at same temperature is realized. Advantage in so doing is quite obvious. Instead of FeO, metal iron was used to split water in another process.[17] Indeed, controlling the extent of reduction reaction to avoid the formation of metal iron is very essential for a steady continuous production of hydrogen as was previously explained.

Molten iron is the key material in the other hydrogen production processes known recently. The HydroMax process contains two steps.[18] First, steam contacts molten iron to form iron oxide and release hydrogen. Second, iron oxide is reduced back to pure metal by adding carbon, a typical metal smelting method. Both steps occur in the same reactor at the same temperature (1250°C). Using water to directly produce pure hydrogen is common with our process. However, the operation cycle is between molten iron and iron oxides; therefore, the operation temperature (1250°C) is much higher than the cycle between FeO and Fe_3O_4 (800°C). Apparently, considerable difference in the energy and investment costs must be generated in the different operation temperatures. The Hymelt Process[19] uses hydrocarbons including coal as the source of hydrogen. The molten iron plays both the role of catalyst for the decomposition of feedstock and the role of solvent for the produced carbon in the first reactor. Oxygen is used to release the dissolved carbon from the molten iron generating CO rich gas in another reactor. The operation temperature (1400–1800°C)[20] is even higher than that of HydroMax process and pure hydrogen cannot be directly obtained. Solid materials have to be dealt with in the molten iron processes. Processing solid materials is a difficult task,[20] and more cost has to be paid compared to process gaseous streams as is in the proposed method.

Conclusions

1. It is experimentally shown that pure hydrogen is produced via the cycle of redox reactions of iron oxides in the assistance of carbon.
2. Three reactions included in the process proceed without the need of catalysis. Both oxidation and reduction reactions of iron oxides proceed at a constant temperature, which favors switching the reaction from one to the other.
3. The reduction of iron oxides experienced different stages. Metal iron as the product of the last stage is better to and can be avoided by tuning the condition of reduction.
4. Water and carbon are consumed for the production of hydrogen, but carbon functions only as the supplier of reducing gas and never react with water, which guarantees the purity of hydrogen.
5. The new process is energetically justified with the TEG value of 3.24. It is also energetically more than autarky and 38% of the produced carbon monoxide can be a by-product of the process.
6. The process operation is quite simple and the operation temperature is quite low compared to the counterpart processes.

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