

# Improvement of methane steam reforming by using equilibrium shift with lithium silicate

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## Abstract

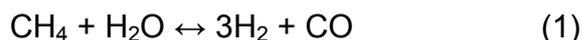
Equilibrium shift is thought to be effective for promoting hydrogen (H<sub>2</sub>) production by methane (CH<sub>4</sub>) steam reforming. Our study clarified the effect of equilibrium shift by using a packed bed reactor with a mixture of reforming catalyst and CO<sub>2</sub> absorbent, resulting in the concentration of H<sub>2</sub> 94 vol% and that of CO 0.16 vol% at atmospheric pressure. In this experiment, lithium silicate (Li<sub>4</sub>SiO<sub>4</sub>), developed by Toshiba, was applied as the absorbent. This absorbent can emit CO<sub>2</sub> rapidly at considerably lower temperature than a well-known absorbent, calcium oxide (CaO). Li<sub>4</sub>SiO<sub>4</sub> is, therefore, considered to be more suitable since required heat for regeneration should be less.

In this work, the effect of equilibrium shift at pressurized condition was studied and the increase in the effect of equilibrium shift was obtained. The concentration of H<sub>2</sub> increased to 96 vol%, and that of CO was kept at a similar value, 0.17 vol% at 300 kPa.

*Keywords:* Hydrogen, Methane steam reforming, Equilibrium shift, CO<sub>2</sub> absorbent, Lithium silicate.

## Introduction

The major process for H<sub>2</sub> production is steam reforming of CH<sub>4</sub>, which is the main component of natural gas and town gas. Equation (1) represents CH<sub>4</sub> reformer's reaction.



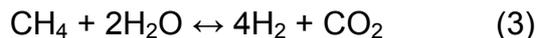
The typical production gas from the reactor contains ca. 75 vol% H<sub>2</sub> and ca. 10 vol% carbon monoxide (CO). Then, this gas is fed to a water-gas shift reactor to reduce CO concentration. Equation (2) represents its reaction.



This part usually consists of two reactors, i.e., a high temperature water-gas shift reactor and a low temperature water-gas shift reactor. The effluent gas from a pair of shift reactors contains some vol% increased H<sub>2</sub> and 0.5-1 vol% CO. This gas is then fed to Pressure Swing Adsorption (PSA) for purification of H<sub>2</sub> in the case of industrial H<sub>2</sub> production or to a preferential oxidation for CO removal in the case of power generation by a fuel cell. Both methods reduce CO concentration to a value lower than 0.001 vol% (10 ppm).

In recent years, a new type of method using equilibrium shift for promoting H<sub>2</sub> production by CH<sub>4</sub> steam reforming has been proposed. This is based on Le Chatelier's principle that a reaction under an equilibrium limitation can be promoted by removing some of the products selectively from the reaction zone. By using this process, it is possible to obtain a larger amount of H<sub>2</sub> and a smaller amount of CO than equilibrium values with a

steam reforming reactor. Equation (3) represents total reaction of (1) and (2).



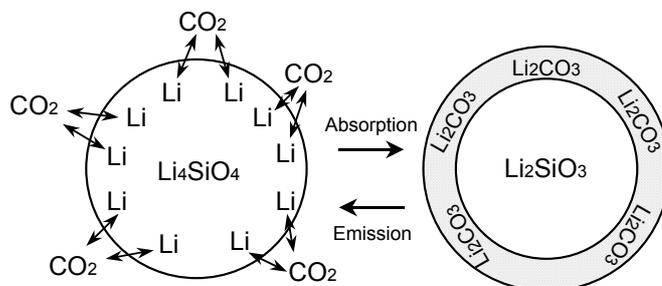
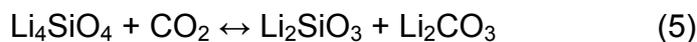
As shown in this equation, two main products exist, i.e.,  $\text{H}_2$  and  $\text{CO}_2$ . Therefore, in order to shift the equilibrium, there are two methods, i.e.,  $\text{H}_2$  removal and  $\text{CO}_2$  removal. In the case of  $\text{H}_2$  removal, a membrane reactor is used, which uses membranes generally made of palladium or palladium alloy to selectively remove  $\text{H}_2$  from the reaction zone. Many studies have been reported on this method and increased conversion of  $\text{CH}_4$  and very high concentration of  $\text{H}_2$  were obtained with a reactor at lower temperature than in the conventional method. Moreover, a  $\text{H}_2$  production system equipped with the membrane reactor has already been developed. The most important points for development of this system are decrease of energy loss due to pressurization for  $\text{H}_2$  permeation and reduction of cost of membrane.

On the other hand, in the case of  $\text{CO}_2$  removal, a packed bed reactor with a mixture of reforming catalyst and  $\text{CO}_2$  absorbent is used to selectively remove  $\text{CO}_2$  from the reaction zone. This kind of process is well known as the Sorption Enhanced Reaction Process and has been studied worldwide<sup>1-3</sup>. Two effects were shown, namely, reduction of  $\text{CO}$  concentration due to promotion of water-gas shift reaction (Equation (2)) and increase of  $\text{CH}_4$  conversion due to promotion of total reaction (Equation (3)). Moreover, these results were obtained at lower temperature than in the conventional method. In this case, energy loss due to pressurization for absorption is very small and cost of absorbent is relatively modest. Therefore, the important point is to decrease energy loss due to supply of heat for regeneration of absorbent, since  $\text{CO}_2$  emission is an endothermic reaction. In most cases, calcium oxide ( $\text{CaO}$ ) is used as  $\text{CO}_2$  absorbent and  $\text{CO}_2$  emission is generally examined at around  $800^\circ\text{C}$  in  $\text{N}_2$ . Equation (4) represents reversible reaction of  $\text{CaO}$ .



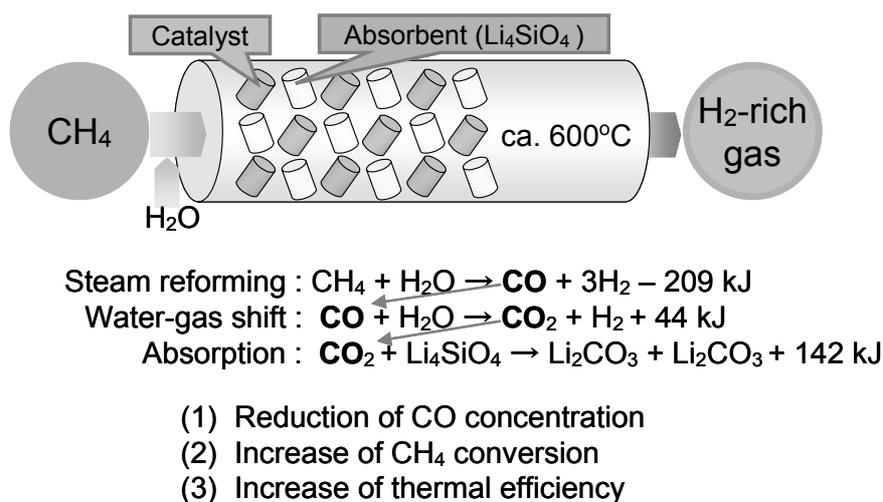
This temperature for regeneration is almost the same as that for conventional steam reforming. Therefore, lowering it is required in order to build a  $\text{H}_2$  production system with high overall efficiency.

A lithium silicate ( $\text{Li}_4\text{SiO}_4$ ) absorbent has been developed as a new  $\text{CO}_2$  absorbent at high temperatures<sup>4-7</sup>. It absorbs  $\text{CO}_2$  at around  $600^\circ\text{C}$  and emits  $\text{CO}_2$  at temperatures above  $720^\circ\text{C}$ , even in the case of pure  $\text{CO}_2$  at 101 kPa. Equation (5) and Fig. 1 represent its reversible reaction for absorption and emission of  $\text{CO}_2$ .



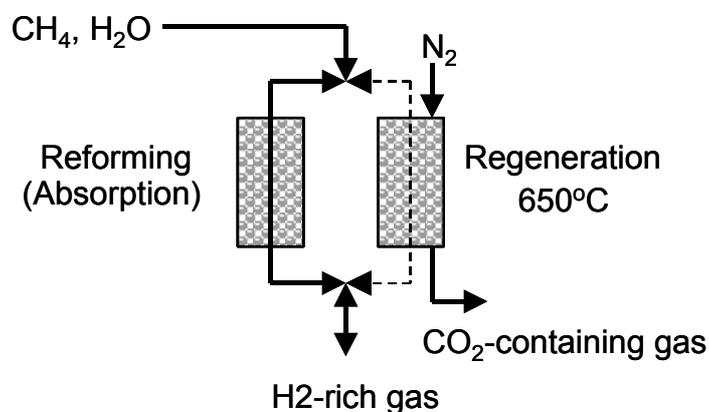
**Fig. 1** Reaction model of  $\text{CO}_2$  absorption and emission by  $\text{Li}_4\text{SiO}_4$

The difference in equilibrium temperature between the two absorbents was calculated to be approximately 200°C on the basis of thermodynamic data<sup>8</sup>. In a gas which does not contain CO<sub>2</sub>, the emission temperature should be reduced because of equilibrium. CO<sub>2</sub> emission of Li<sub>4</sub>SiO<sub>4</sub> in N<sub>2</sub> after full absorption was examined and it completely finished within 0.5 hours at 650°C, which is about 150°C lower than the case of CaO<sup>9</sup>. Since Li<sub>4</sub>SiO<sub>4</sub> has a considerably lower temperature for CO<sub>2</sub> emission than CaO absorbent does, the reaction between Li<sub>4</sub>SiO<sub>4</sub> and CO<sub>2</sub> is easily reversible. Our previous experiments have clarified that a Li<sub>4</sub>SiO<sub>4</sub> pellet has high reversibility, achieving a retention ratio of more than 80% for 20 cycles even in pure CO<sub>2</sub> at 850°C, which was stable after 5 cycles<sup>10</sup>. Therefore, Li<sub>4</sub>SiO<sub>4</sub> is believed to be one of the best absorbents for equilibrium shifting. Figure 2 shows a model and expected effects of packed bed reactor with a mixture of reforming catalyst and Li<sub>4</sub>SiO<sub>4</sub> absorbent.



**Fig. 2** A model for equilibrium shift by using Li<sub>4</sub>SiO<sub>4</sub>

Since CH<sub>4</sub> steam reforming is an endothermic reaction and CO<sub>2</sub> absorption is an exothermic reaction, thermal efficiency is also expected to be increased by performing these two reactions at the same time in a reactor. Moreover, by using two reactors as shown in Fig. 3, a continuous H<sub>2</sub> production system can be built.



Reforming and regeneration are changed every 30 minutes

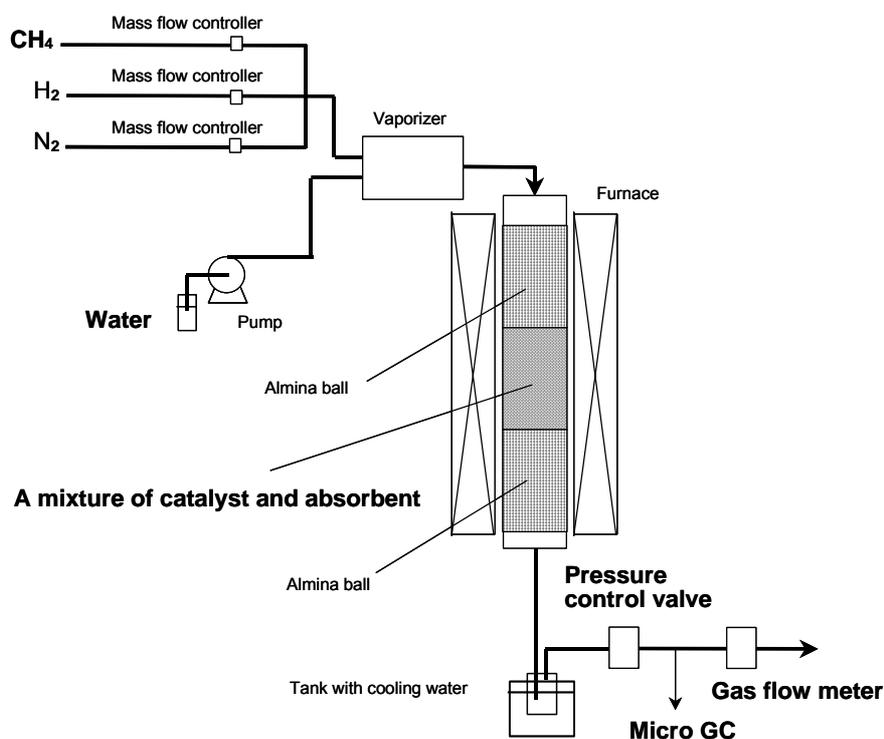
**Fig. 3** Schematic drawing of the continuous H<sub>2</sub> production system

The Effect of equilibrium shift on CH<sub>4</sub> steam reforming with Li<sub>4</sub>SiO<sub>4</sub> was investigated at atmospheric pressure<sup>11</sup> and resulted in the concentration of H<sub>2</sub> 93.7 vol% and that of CO 0.16 vol%. On the other hand, there are some cases, which require reforming under pressurized condition. For example, in a practical purified H<sub>2</sub> production system, pressurized H<sub>2</sub> gas from a reformer is required in order to connect to PSA. In the case of the reformer with equilibrium shift, raising pressure is expected to bring about two conflicting effects. It can promote CO<sub>2</sub> absorption to obtain larger effect of equilibrium shift. On the other hand, it can suppress CH<sub>4</sub> steam reforming reaction on the basis of equilibrium. In this work, the equilibrium shift effect for steam reforming of CH<sub>4</sub> by using Li<sub>4</sub>SiO<sub>4</sub> at pressurized condition was studied.

## Experimental

Commercially available steam reforming nickel catalyst was used, which was cylindrical pellet with diameter of 3 mm and length of 3 mm. The Li<sub>4</sub>SiO<sub>4</sub> pellets used as CO<sub>2</sub> absorbent were spherical pellets with average grain size of 5 mm. The pellets consist mainly of lithium silicate, with some additives for promotion of CO<sub>2</sub> absorption and suppression of degradation during the absorption-emission cycles.

Figure 4 shows experimental apparatus for reforming. A mixture of steam reforming catalyst and CO<sub>2</sub> absorbent was placed in a metal reactor that has 21 mm inner diameter. Height of packed bed was around 320 mm. Packed beds of alumina balls were placed on and under this packed bed with each bed having a height of around 300 mm, in order to promote uniform gas diffusion and temperature in the bed of the mixture. For comparison, the test for the case of catalyst alone was also performed, using a mixture of catalyst and alumina ball, in which amount of catalyst and bed height of the mixture were the same as in the case of catalyst and absorbent. The reactor was heated by electric furnace. The feed gases were introduced from the top and removed from the bottom.



**Fig. 4** Apparatus for steam reforming experiment

Initially, the reactor was heated to 600°C in a gas flow of N<sub>2</sub>. Next, H<sub>2</sub> was mixed with N<sub>2</sub> to reduce the catalyst. After 30 minutes, H<sub>2</sub> was switched to steam and the temperature was kept at 600°C. Then, total pressure was increased and kept at 300 kPa with pressure control valve and N<sub>2</sub> was switched to CH<sub>4</sub> to start the steam reforming process. Steam reforming was continued for 30 minutes at 600°C. Space velocity, expressed as the catalyst volume to the feed gas flow rate, was 2000 h<sup>-1</sup>.

Three conditions were decided based on a consideration of practical conditions. Firstly, the pellets are comparatively large, since in the case of packing small pellets or granules, pressure drop in the practical reactor increases and energy for introducing reactant gas increases. Secondly, steam/carbon ratio, which is equal to H<sub>2</sub>O/CH<sub>4</sub> ratio in this case, was 4.0, which is similar to the value in an actual H<sub>2</sub> production system. Finally, no carrier gas such as nitrogen (N<sub>2</sub>) was mixed with reactant gas, since it reduces H<sub>2</sub> concentration and is not considered to be used in a practical apparatus.

## Results and Discussion

As a result of the test, CO<sub>2</sub> concentration was kept at 0.07 vol% or below for 30 minutes. This value is smaller than the equilibrium value, 14 vol%. Similarly, CO concentration was kept at 0.17 vol% or below. This is also smaller than the equilibrium value, 4.6 vol%. It is obvious that reduction of CO<sub>2</sub> due to absorption resulted in promotion of water-gas shift reaction (Equation (2)) by equilibrium shift to reduce CO concentration. Furthermore, it is possible to dispense with a CO-shift reactor and simplify PSA apparatus, as CO concentration was less than 0.5 vol%.

H<sub>2</sub> concentration was kept at 95.6 vol%, which is higher than equilibrium value, 71 vol%, as shown in Fig. 5. The effect of equilibrium shift on promoting CH<sub>4</sub> steam reforming reaction (Equation (1)) was observed clearly. This high concentration of H<sub>2</sub> can cause increase of efficiency of PSA and overall efficiency at H<sub>2</sub> production. According to the above, a simple and efficient H<sub>2</sub> production system is expected to be established.

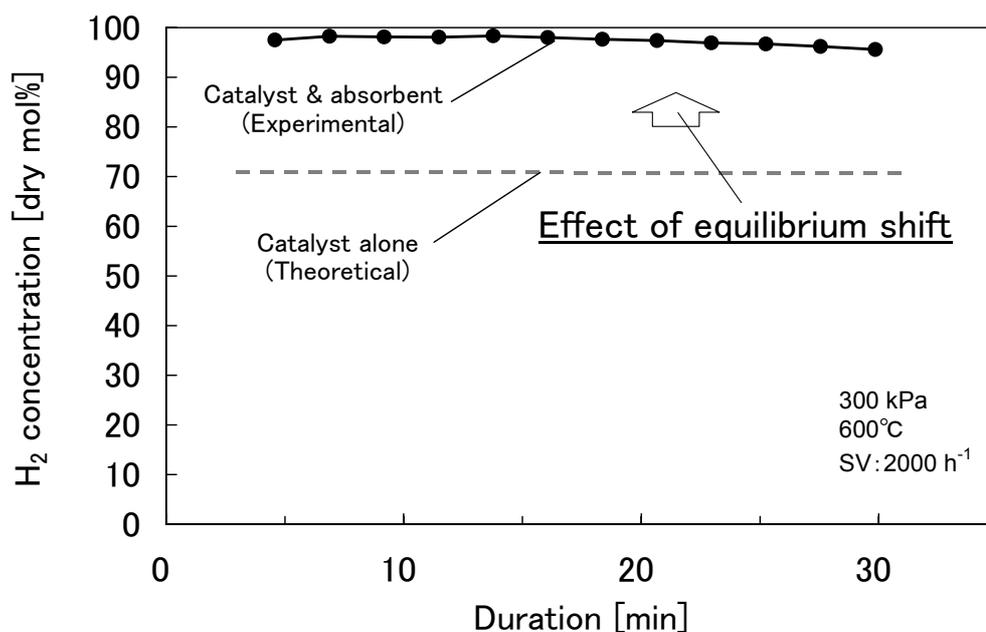


Fig. 5 H<sub>2</sub> concentration as a function of time

## Conclusion

The effect of equilibrium shift for CH<sub>4</sub> steam reforming by using Li<sub>4</sub>SiO<sub>4</sub> at pressurized condition, 300 kPa, was investigated with a view to expanding application. The concentration of H<sub>2</sub> was 96 vol%, and that of CO was 0.17 vol%. It was concluded that equilibrium shift reforming with Li<sub>4</sub>SiO<sub>4</sub> can be performed under pressurized condition.

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