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Effect of equilibrium-shift in the case of using lithium silicate pellets in ethanol steam reforming

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ABSTRACT

Ethanol is a renewable biomass-derived fuel. It seems, therefore, to be one of the most suitable raw materials for the production of hydrogen. Steam reforming can be utilized for hydrogen production and equilibrium shifting is considered to be effective for promoting the reaction. Our group has succeeded in removing the CO_2 by-product selectively from the reaction zone by using a packed bed reactor with a mixture of a steam-reforming catalyst and a CO_2 absorbent. Pellets of lithium silicate (Li_4SiO_4) were applied as the absorbent. This is a report on the relationship between CO_2 absorption by Li_4SiO_4 and the equilibrium-shift effect for overall reactions. Experimental results showed an obvious effect that resulted in keeping not only the concentration of H_2 above 99 dry vol% but also the concentration of CO below 0.12 dry vol% for 0.5 h.

1. Introduction

Use of ethanol (C_2H_5OH) is expected to increase greatly, since it is a biomass-derived renewable fuel. Moreover, it is considered to be one of the best candidates as a new raw material for the production of hydrogen (H_2), whereas currently one of the most common raw materials for production of H_2 is methane (CH_4), which is the main component of natural gas, i.e., a fossil fuel [1]. H_2 production from biomass ethanol will realize a system, in which biomass is finally used for a wide range of applications, as shown in Fig. 1. This system can reduce the use of fossil fuel and the emission of CO_2 to the atmosphere.

In the case of using C_2H_5OH for H_2 production, a steam reforming method is considered to be suitable as in the case of using CH_4 and many works have been reported [2–7]. Recently, a new method using equilibrium shifting for promoting H_2 production by 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. Removed product is mostly chosen from two materials, i.e., H_2 and CO_2. In the case of CO_2 removal, a packed bed reactor with a mixture of a steam-reforming catalyst and a CO_2 absorbent is generally used to selectively remove CO_2 [8–19]. In this process, the important point is to decrease energy loss due to the supply of heat for regeneration of the absorbent, since CO_2 emission is an endothermic reaction. Therefore, lowering the regeneration temperature is considered to be necessary to build a H_2 production system with high overall efficiency. Based on this idea, our group has developed a lithium silicate (Li_4SiO_4) absorbent as a new CO_2 absorbent at high temperatures [20–26]. Eq. (1) represents its reversible reaction.

$$Li_4SiO_4 + CO_2 \rightleftarrows Li_2SiO_3 + Li_2CO_3 \quad (1)$$

High reversibility of the Li_4SiO_4 pellet (5 mm) in the absorption–emission cycle was confirmed by the flow

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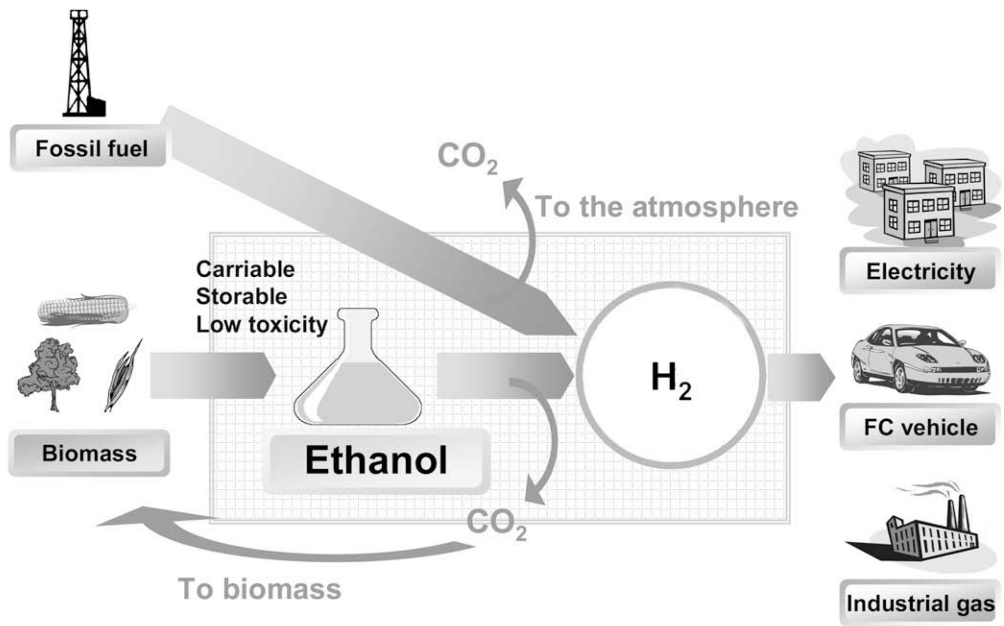

Fig. 1 – Concept for use of H_2 converted from biomass ethanol.

condition of dry CO_2 for absorption and N_2 for emission. Furthermore, CO_2 emission of the pellet in N_2 after full absorption finished within 0.5 h at 923 K, which is about 150 K lower than in most cases of the well-known absorbent, CaO [27].

Promotion of C_2H_5OH steam reforming by removing CO_2 with Li_4SiO_4 granules (*ca.* 0.7 mm) was reported [28,29]. Eq. (2) represents the overall reaction of C_2H_5OH steam reforming.

$$C_2H_5OH + 3H_2O \rightleftarrows 6H_2 + 2CO_2 \quad (2)$$

In this reaction, other by-products, mainly CO and CH_4, exist. The amount of CO was reduced due to the promotion of Eq. (3) by removing CO_2 and the amount of CH_4 was also reduced due to the promotion of Eq. (4) as a result of the reduction of CO concentration.

$$CO + H_2O \rightleftarrows H_2 + CO_2 \quad (3)$$

$$CH_4 + H_2O \rightleftarrows 3H_2 + CO \quad (4)$$

Consequently, higher H_2 concentration was obtained than that by the conventional method. The produced gas by reforming is generally fed to a CO-shift reactor, which reduces CO by applying Eq. (3) and CO concentration of the effluent gas is reduced to 0.5–1.0 dry vol%, typically. This gas is then fed through a pressure swing adsorption (PSA) process for purification of H_2 or to a CO removal reactor by using preferential oxidation. Therefore, if CO concentration is reduced to the value below 0.5 dry vol% due to the promotion of C_2H_5OH steam reforming by removing CO_2, it is possible to dispense with the CO-shift reactor.

In this work, Li_4SiO_4 pellets were used as a CO_2 absorbent, considering a practical apparatus for H_2 production, and the relationship between CO_2 absorption by Li_4SiO_4 and the equilibrium-shift effect for steam reforming of C_2H_5OH was studied. The influence of temperature, which has a strong relationship to the absorption property, on the composition of the produced gas was investigated in the temperature range from 800 to 900 K. This is the same temperature range as in the case of using CH_4 as the raw material [18], and is expected to be suitable for equilibrium shifting. In deciding the experimental conditions, practical apparatus for a H_2 production system was considered.

2. Experimental

Considering practical conditions, it was decided to apply three conditions. Firstly, the pellets were 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, the H_2O/C_2H_5OH ratio was 6.0, which was just twice the stoichiometric value and comparatively small among the results of previous research into C_2H_5OH steam reforming at similar temperatures. Finally, only 5 vol% of nitrogen (N_2) carrier gas was mixed with reactant gas, since it reduces practical concentration of produced H_2. In many reports, carrier gas is used in the range between 10 and 94 vol%. However, in a practical apparatus, it is thought that it should be smaller or even 0 vol% in order not to reduce H_2 concentration from the reformer. This 5 vol% carrier gas was used to avoid condensation by smoothly flowing the reactant vapor.

Ten grams of commercially available steam-reforming Ni/Al_2O_3 catalyst (Ni content: 58 wt%, N186(3), Nikki Chemical Co., Ltd.) was used, which was in the form of cylindrical pellets with diameter of 3 mm and length of 3 mm. Sixty grams of the Li_4SiO_4 pellets, which were in the form of spherical pellets with average pellet size of around 5 mm (LS-HE906, Toshiba Ceramics Co., Ltd.), was used as the CO_2 absorbent. The pellets consist mainly of Li_4SiO_4, with some