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# Application of one-body hybrid solid pellets to sorption-enhanced water gas shift reaction for high-purity hydrogen production

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ABSTRACT

Interest in hydrogen, regarded as a new clean energy carrier, has been increasing with expectation of the approaching hydrogen economy. In the hydrogen economy, hydrogen will replace the conventional fuels that have caused pollution problems. As one of the methods for the mass production of hydrogen, water gas shift (WGS) reaction ($CO + H_2O \leftrightarrow H_2 + CO_2$) has been highlighted for synthesis gas feed, which is produced by coal and biomass gasification. Recently, the performance of WGS reaction has been improved significantly through application of the sorption-enhanced WGS (SE-WGS) reaction concept, where WGS reaction and $CO_2$ sorption are carried out simultaneously. High-purity hydrogen can be directly produced through the SE-WGS reaction, without need for further purification processes. In the SE-WGS reaction, uniform packing of the mixture of catalyst and sorbent is important; however, this is difficult to manage with conventional catalyst and sorbent pellets. In this study, novel one-body hybrid solid pellets consisting of the mixture of catalyst and sorbent were prepared to address this shortcoming and applied to SE-WGS reactions. From experiments, the effect of different ratio of catalyst/sorbent in one-body hybrid solid pellets was studied. A novel multi-section packing concept was also applied to SE-WGS reaction with one-body hybrid solid pellets. The experimental results showed that one-body hybrid solid pellets can be successfully used and that multi-section packing can increase the hydrogen productivity in SE-WGS reaction.


## Introduction

Due to the excess use of fossil fuels, serious global environmental issues such as climate change and pollution have arisen [1]. With the awareness of these problems, there have been efforts for reductions in fossil fuel usage. However, fossil fuels are still our main source of energy, and about 80% of the world's commercial energy is produced from them [2]. As a potential solution to environmental problems relating to energy production, hydrogen has been receiving more and more interest. Hydrogen has been considered as an alternative

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energy carrier since the 19th century [3], because hydrogen is an environmentally benign fuel in that only water is released when hydrogen is burned or converted into other types of energy such as electricity. In addition, hydrogen exhibits the highest heating value per mass among all chemical fuels [4]. Hydrogen already has been used for various industrial applications, for example, chemical processes such as ammonia, urea, and methanol synthesis and crude oil upgrading by hydrocracking and hydrotreating. At present, the total world production of hydrogen is approximately 50 million tons per year [5].

As one of the methods for bulk production of hydrogen, water gas shift (WGS) reaction has been highlighted for synthesis gas feed which is produced by gasification of carbonaceous feedstocks such coal and biomass [6]. Especially, because coal is relatively cheap and abundant compared with other carbonaceous feedstocks, coal conversion technologies are highly desirable for efficient and economical production of hydrogen [7]. In the WGS reaction, steam and carbon monoxide react and produce hydrogen and carbon dioxide ($CO + H_2O \leftrightarrow H_2 + CO_2$). The WGS reaction is exothermic, therefore the equilibrium composition of reactants CO and $H_2O$ increases and that of products $H_2$ and $CO_2$ decreases with increasing reaction temperature (Fig. 1). For high-purity hydrogen production, byproduct $CO_2$ and unreacted feed gases need to be removed through additional separation processes such as pressure swing adsorption (PSA) [9]. Recently, it was shown that the performance of WGS reaction can be significantly improved by applying the sorption-enhanced reaction concept, in which WGS reaction and $CO_2$ removal by sorption are carried out simultaneously in a single unit operation [10–16]. Through sorption-enhanced WGS (SE-WGS) reaction, the thermodynamic equilibrium limitation of the WGS reaction can be circumvented through Le Chatelier's principle, resulting in direct production of high-purity hydrogen at high temperature in a compact process, without need for further purification steps.

In the SE-WGS reaction, to carry out a WGS reaction and $CO_2$ sorption simultaneously, the uniform packing of the mixture of catalyst and sorbent is essential (Fig. 2a). However, uniform packing is not easily manageable with conventional catalyst and sorbent pellets. To overcome the unequally distributed solid packing problem, a one-body hybrid solid consisting of catalyst and sorbent can be applied to the SE-WGS reaction (Fig. 2b). The one-body hybrid solid is either a single pellet form made of well-mixed catalyst and sorbent in a regular ratio or a composite having dual functions of catalysis and sorption [17–19]. By using the one-body hybrid solid pellets, catalyst and sorbent can be uniformly packed in a column.

In this study, one-body hybrid solid pellets with different ratios of catalyst and sorbent were prepared and experimentally tested in SE-WGS reactions. $K_2CO_3$-promoted hydrotalcite and commercial WGS catalyst were used as $CO_2$ sorbent and catalyst, respectively. The $K_2CO_3$-promoted hydrotalcite has been widely tested and used as a high-temperature $CO_2$ sorbent because it has a relatively high $CO_2$ sorption capacity, fast sorption kinetics, and good cyclic stability at high temperatures of 200–400 °C [20–23]. Also, the multi-section packing concept, which was suggested to improve the SE-WGS reaction performance, was tested with one-body hybrid solid pellets. In the multi-section packing concept, a reactor column is divided into more than two sections, and the catalyst and sorbent are packed into each section at different ratios (Fig. 2c), offering more flexibility in operation [24].

## Experiments

### *WGS catalyst and $CO_2$ sorbent*

To demonstrate WGS and SE-WGS reactions experimentally, commercial WGS catalyst ($Cu/ZnO/Al_2O_3$, Sud-Chemie) and synthesized $CO_2$ sorbent, potassium carbonate ($K_2CO_3$, Sigma-

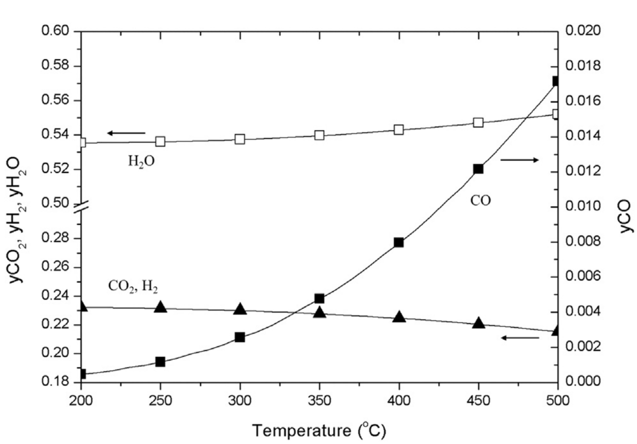


**Fig. 1 – Equilibrium gas compositions of WGS reaction for $H_2O$/CO feed mole ratio of 3:1 at 1 atm and different temperatures. The equilibrium reaction constant is from Twigg (1987) [8].**

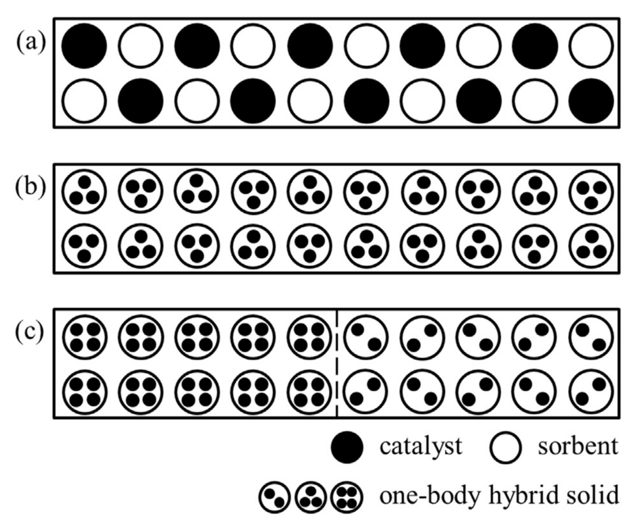


**Fig. 2 – Different packing concepts of the mixture of catalyst and sorbent in an SE-WGS reaction column; (a) ideal conventional packing, (b) packing with one-body hybrid solid containing both catalyst and sorbent, and (c) multi-section packing with one-body hybrid solid.**