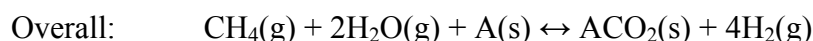
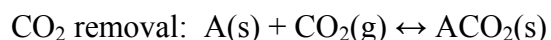
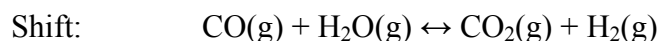
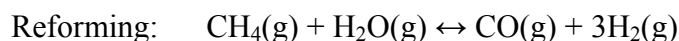


420d The Selection and Preparation of High Temperature Novel CO₂ Sorbents

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Sorption-enhanced reforming (SER) accomplishes reforming, shift, and purification in a single processing step. The reactions occur simultaneously in the presence of reforming catalyst and a CO₂ sorbent (notated as A) [1]. The simultaneous and overall reactions are



Removal of CO₂ takes very important role in this reaction. It shifts the normal equilibrium limits of the reforming and shift reactions and permits high CH₄ conversion with almost complete removal of CO and CO₂. Recently, importance of selecting this high temperature CO₂ sorbent gained attention with respect to performing long-term multi-cycle. Currently, the most widely used high temperature CO₂ sorbent is dolomite. It is a natural mineral and its most attractive feature is cheap price. However, normally natural dolomite contains small amount of sulfur, which is enough deactivate catalyst. In order to utilize dolomite, energy intensive pretreatment has to be performed prior to loading. In addition, it has tendency to decrease capacity significantly through multi-cycle [2].

Therefore, a new generation of high temperature CO₂ sorbents such as Li₄SiO₄[3], Li₂ZrO₃, K doped Li₂ZrO₃[4], and Na₂ZrO₃[5] are developed sorbents recently. However, multi-cycle durability has not been proved using Li₄SiO₄. Li₂ZrO₃ has shown slow kinetics. Also, when K is doped on Li₂ZrO₃, one may obtain faster kinetics but will lose CO₂ capacity by the amount occupied by K₂CO₃. Na₂ZrO₃ showed fast kinetic and stable weight gain but original weight is not obtained after first regeneration.

In this study, new CO₂ sorbents including those listed above was selected through thermodynamic screening using commercial software (HSC chemistry). Alkali metals such as Li, Na, and Ca were combined with other metal oxides and resulting compounds were put in condition of SER. Then, hydrogen yields were obtained through calculation of the software. The compounds providing more than 95% of hydrogen yield in the range of 500°C to 700°C were selected. The selected materials were Li₂ZrO₃, Na₂ZrO₃, Na₂Fe₂O₄, Na₄SiO₄, Ca₂Al₂O₅, and Ca₃Al₂O₅. These six materials were prepared in various ways in laboratory.

It can be divided to two major preparation methods. One is solid-solid reaction method; the other is liquid based method with various precursors. Most of materials were prepared successfully and its chemical compositions were identified with XRD. Its surface areas were measured with custom designed and calibrated BET equipment. Its surface morphology was identified using SEM. Then, prepared materials were tested in thermogravimetric analyzer (TGA).

While Li_2ZrO_3 prepared using solid-solid reaction showed very slow kinetics, Li_2ZrO_3 prepared using liquid based method showed faster kinetics ($38 \text{ mgCO}_2/\text{g}\cdot\text{min}$), large capacity ($26 \text{ g CO}_2/100 \text{ g sorbent}$) and stable multi-cycle result. Its CO_2 uptake rate was faster than any other Li_2ZrO_3 reported. Also, small particle size of Li_2ZrO_3 allows avoiding doping of K.

Na_2ZrO_3 showed similar CO_2 uptake rate with both preparation methods. However, liquid based preparation provided full recovery of original weight with fast kinetics after regeneration while the one with solid based preparation method showed 10% of loss of its capacity.

Furthermore, rest of materials were tested and showed general favor of liquid based preparation method.

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