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 CO_2 sorbent (notated as A) [1]. The simultaneous and overall reactions are

Reforming: $CH_4(g) + H_2O(g) \leftrightarrow CO(g) + 3H_2(g)$

Shift: $CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g)$

CO_2 removal: $A(s) + CO_2(g) \leftrightarrow ACO_2(s)$

Overall: $CH_4(g) + 2H_2O(g) + A(s) \leftrightarrow ACO_2(s) + 4H_2(g)$

Removal of CO_2 takes very important role in this reaction. It shifts the normal equilibrium limits of the reforming and shift reactions and permits high CH_4 conversion with almost complete removal of CO and CO_2. Recently, importance of selecting this high temperature CO_2 sorbent gained attention with respect to performing long-term multi-cycle. Currently, the most widely used high temperature CO_2 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 CO_2 sorbents such as Li_4SiO_4[3], Li_2ZrO_3, K doped Li_2ZrO_3[4], and Na_2ZrO_3[5] are developed sorbents recently. However, multi-cycle durability has not been proved using Li_4SiO_4. Li_2ZrO_3 has shown slow kinetics. Also, when K is doped on Li_2ZrO_3, one may obtain faster kinetics but will lose CO_2 capacity by the amount occupied by K_2CO_3. Na_2ZrO_3 showed fast kinetic and stable weight gain but original weight is not obtained after first regeneration.

In this study, new CO_2 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 $500^{o}C$ to $700^{o}C$ were selected. The selected materials were Li_2ZrO_3, Na_2ZrO_3, $Na_2Fe_2O_4$, Na_4SiO_4, $Ca_2Al_2O_5$, and $Ca_3Al_2O_5$. 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 mgCO_2/g·min), large capacity (26g CO_2/ 100g 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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