



Fly ash derived lithium silicate for in-situ pre-combustion CO₂ capture

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Abstract

Steam gasification process converts biomass into a mixture of CO, CO₂, CH₄, and H₂. Biomass gasification at temperatures as low as 500 °C can be achieved by using appropriate catalysts [1]. During gasification, the reversible water gas shift (WGS) reaction continues until reaching equilibrium and decreases with increasing temperature [2]. An effective strategy to drive the WGS reaction forward is to take out CO₂ from the product mixture by combining H₂ production and capture of CO₂, i.e. sorption-enhanced steam gasification of biomass [3]. Through in-situ CO₂ capture, H₂ production can be achieved at lower temperatures than the traditional gasification process (550 °C instead of 800 °C); which lowers energy requirement, coking and sintering of catalyst and capital expenditure [3,4]. Therefore, there is a need to conduct in-situ removal of CO₂ under gasification conditions at low temperature (~500°C), since most of the work reported using CaO sorbents is at high temperatures [3,5].

In this work, a fly ash derived lithium silicate material (Li-FA) developed at Heriot-Watt University was tested for the simultaneous removal of CO₂ using simulated syngas at low gasification temperature at the University of Utah. The CO₂ uptake tests at high pressure were carried out using a high pressure thermogravimetric system at 380°C and 500°C, 15 bar and simulating a synthetic biomass derived syngas mixture. The SS316 sample holder was designed for samples with particle size > 150 µm, so that the starting lithium silicate powder was screened to select particles larger than 150 µm. Before the CO₂ uptake tests, the material was firstly run in presence of 50% H₂O, 30% H₂, 20% N₂ at 15 bar to desorb any water from the surface. It was observed that the weight decreased about 7%, indicating that no sorption of H₂/H₂O occurred. The tests confirmed that the material is able to absorb CO₂ at 380°C (1.2 mmol CO₂ / g sorbent) and 500°C (2.77 mmol/g) in presence of 50% H₂O, 30% H₂, 20% CO₂ at 15 bar. Desorption studies were carried out at 15bar switching from CO₂ to N₂, and it was found that the desorption was not completed (75% completed) under these conditions. This indicates that pressure swing process or a higher desorption temperature are required for complete desorption.

XRD analysis (X'Pert³ Powder) of the parent Li-FA sample and after CO₂ sorption/desorption cycles were carried out. The main mineral phases identified in the parent sample were tetralithium silicate, Li₄SiO₄ (85%) and lithium catena-silicate, Li₂SiO₃ (15%). The XRD of the material after CO₂ sorption/desorption shows that the Li₄SiO₄ phase decreased to 68%, whilst the Li₂SiO₃ phase increased to 32%. Above 262°C, Li₄SiO₄ absorbs CO₂ to form Li₂SiO₃ and Li₂CO₃ [6]. The calculated amount of Li₂SiO₃ that can be related to presence of Li₂CO₃ in the used Li-FA (17%) confirms that some Li₂CO₃ is present in the material due to incomplete desorption under the tested conditions, which is in agreement with the thermogravimetric results. In summary, Li-FA may be an efficient CO₂ sorbent under pre-combustion conditions since it is not affected by the presence of H₂

and H₂O, but further work is required to achieve complete regeneration and establish its stability over a larger number of cycles.

References

- [1] M. Asadullah, S.I. Ito, K. Kunimori, M. Yamada, K. Tomishige, Biomass Gasification to Hydrogen and Syngas at Low Temperature: Novel Catalytic System Using Fluidized-Bed Reactor, *J. Catal.*, 2002, 208, 255–259.
- [2] M. Rosen, D. Scott, Comparative Efficiency Assessment for a range of hydrogen production processes, *Int. J. Hydrogen Energy*, 1998, 23, 653-659.
- [3] S. Danaei Kenarsari, Y. Zheng, CO₂ capture using calcium oxide under biomass gasification conditions, *Journal of CO₂ Utilization*, 2015, 9, 1-7.
- [4] N.H. Florin, A.T. Harris, Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents, *Chem. Eng. Sci.*, 2008, 63, 287-316.
- [5] Z.-s. Li, N.-s. Cai, Y.-y. Huang, Effect of Preparation Temperature on Cyclic CO₂ Capture and Multiple Carbonation–Calcination Cycles for a New Ca-Based CO₂ Sorbent, *Ind. Eng. Chem. Res.*, 2006, 45, 1911-1917.
- [6] Y. Duan, H. Pfeiffer, B. Li, I.C. Romero-Ibarra, D. C. Sorescu, D.R. Luebke and J.W. Halley, CO₂ capture properties of lithium silicates with different ratios of Li₂O/SiO₂: an ab initio thermodynamic and experimental approach, *Phys.Chem. Chem. Phys.*, 2013, 15, 13538.