	Experiment title: **In operando Alkali ions and carbonates redistribution in Alumina based CO_2 sorbent**	Experiment number: **26-01- 869**
Beamline: SNBL	**Date(s) of experiment**: 14-19 July 2009	**Date of report**: 23-09-2010
Shifts: 12	**Local contact(s)**: Wim Bras (Dubble)	

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Background and strategy

Hydrotalcite (HT) based materials $M_x^{2+}M_{1-x}^{3+}(OH)_2(CO_3)_{\frac{1-x}{2}}\cdot yH_2O$, comprising Mg and Al, are currently being investigated as CO_2 sorbents for pre-combustion carbon capture in coal fired power plants to reduce greenhouse gas emissions [1]. In parallel with successful sorption enhanced water gas shift bench scale demonstration at ECN, adsorption of CO_2 on hydrotalcite and K_2CO_3 promoted HT needs to be thoroughly studied at relevant pressures and temperatures for further optimisation of the performance of sorbent materials. Critical parameters are bulk carbonate formation/decomposition, segregation MgO($MgCO_3$) and Ga_2O_3 (Al_2O_3), the alkali loading and dispersion throughout Mg,Ga(Al) oxide matrix. Previous experiments carried out at Swiss Norwegian Beam Lines (SNBL) thanks to shift exchange program with DUBBLE allowed us to develop a gas cell that is suitable for in-operando studies of sorbent materials for Sorption-Enhanced Water-Gas shift. Besides, the experimental XRD data gathered allowed us to identified several bulk processes occurring upon adsorption of CO2 in the presence of steam [2,3].
In situ high resolution XRD and XAS give insights on local coordination changes of Mg/Al(Ga) during thermal decomposition and CO_2 ad/desorption cycles under 10bars steam:CO_2 (high pressure experimental setup at DUBBLE). Furthermore, structural rearrangement of the material bring useful information about the nature of adsorption sites and the role of alkali promoters. In our samples Ga replaced Al (XAS for Ga K-edge). Experimental strategy included the study of both K_2CO_3 promoted and non-promoted Ga- substituted hydrotalcites with Mg/Ga ratio of 2.9 and 0.5.

Results obtained at DUBBLE in July 2010

The high temperature/high pressure gas cell used in these experiments is the one from SNBL that had been used in 26-01-839, heat tracing has been checked thoroughly to avoid condensation of water.

Non promoted Ga,Mg HT (Mg/Ga 2.9) was first heated from RT to 400ºC in

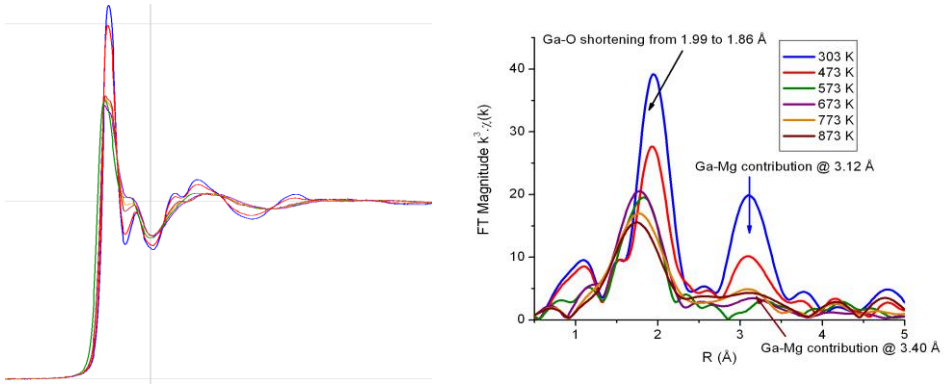

Figure 1: Ga K-edge XANES (LHS) and corresponding EXAFS data (RHS) recorded during heat treatment (RT to 400ºC) in CO_2 of Ga,Mg HT* with Mg/Ga 2.9. Note that the colours correspond between the two plots.

a flow of CO_2, and analysed both by XRD and XAS. The XRD showed HT structure from RT to 200, collapsed HT structure from 200 to 300 and ill-defined periclase Mg(Ga)O phase above 300-400ºC. Figure 1 shows the corresponding XANES and EXAFS plot of the Ga K-edge data at various stages of heat treatment.
The initial phase is consistent with the presence of Ga-O (approx. 6) @ 1.99 Å and a shell of a similar number of Mg @ 3.12 Å in good agreement with previously published data for Ga-Mg distances in HTCs [4]. Temperature increase results in a decrease in Ga-O bond length and coordination number and concomitant increase in Ga-Mg distance. The Ga-Mg distance seems typical of the formation of an inverse spinel phase with a predominance of Ga occupying the A site [5]. Interestingly however, the coordination number for Ga-Mg remains very small and is consistent with the lack of long-range order for the spinel phase (absence of reflections in the XRD pattern). The experiment has been the carried out in the presence of high pressure steam and CO_2 and XAS data have been generated for all the sample mentioned above.

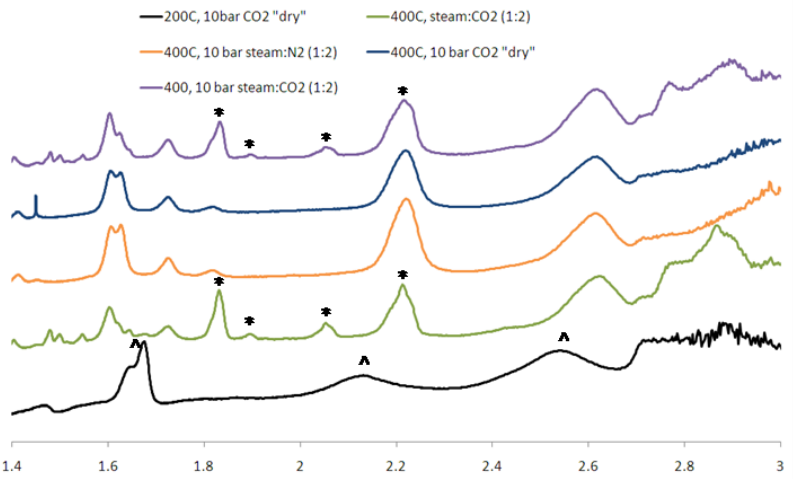

Figure 2: XRD pattern (in d-space) of K_2CO_3 promoted Ga,Mg HT (Mg/Ga 2.9) under various conditions. ^: hydrotalcite *:$MgCO_3$

Our previous study at ESRF has shown that commercial alkali promoted HT transforms to $MgCO_3$ crystalline phase between 300-400°C under CO_2-steam (10 bar 1:1) conditions [2]. Importantly this result has been reproduced with alkali promoted Ga-substituted HT (Mg/Ga 2.9) (figure 2). In contrast non-promoted Ga substituted HT did not show any magnesium carbonate formation as expected from precedent in-house TGA results. Full cycles of adsorption (at 10 bars CO_2/steam) and desorption at 1 bar N_2 dry have further been carried out for each samples and XAS data will be published in a peer-reviewed article which will both discuss the role of Mg/Ga ratio and the role of alkali ions on CO_2 adsorption performance.

Experimental setup

- Despite failure of DUBBLE XRD detector just before the allocated shift, an emergency CCD detector could have been placed by DUBBLE staff by the end of the first shift. XRD data gathered by this way could guarantee reliability and reproducibility of experiments.
- use of high pressure gas cell kindly provided by SNBL was possible after few minor modifications at DUBBLE.
- condensation of steam could be avoided after careful tracing of gas pipes with heating tape. Original commercial tracing was optimally not designed.
- Steam generator which consists of a pressurized liquid water tank and a Liquid Flow Controller has been made more user-friendly by editing a new user manual and by giving practical course to DUBBLE staff.
- Available gas rig was flexible enough to provide desired gas mixture and switch from adsorption to desorption conditions within a reasonable timeframe.

[1] E.R. van Selow et al. Ind. Eng. Chem. Res., 2009, 48, 4184-4193
[2] S. Walspurger, P.D. Cobden, O.V. Safonova, Y. Wu, E.J. Anthony, Chem. Eur. J., 2010, doi 10.1002/chem.201000687
[3] S. Walspurger, P.D. Cobden, W.G. Haije, R. Westerwaal, G.D. Elzinga, O.V. Safonova, Eur. J. Inorg. Chem., 2010, 2461-2464
[4] J. E. Weidenborner, N. R. Stemple, Y. Okaya Acta Cryst., 1966, 20, 761-764
[5] M. Bellotto,B. Rebours, O. Clause, J. Lynch, D. Bazin, E. Elkaim J. Phys. Chem., 1996, 100, 8527-8534