



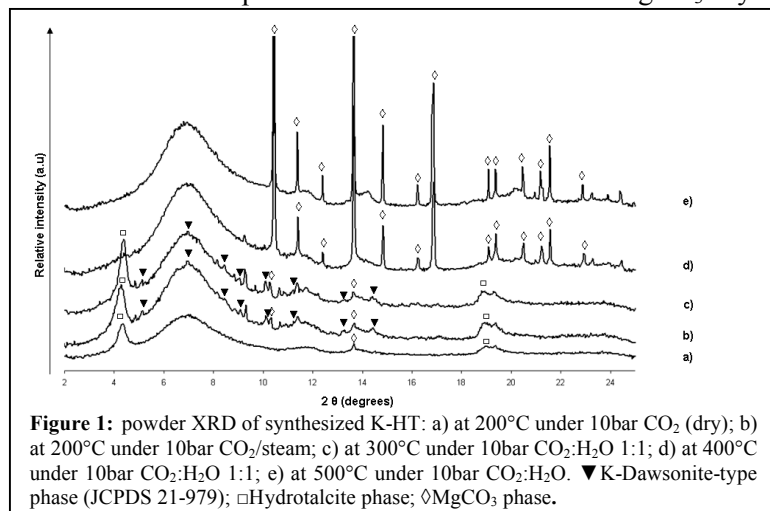
	Experiment title: Hydrotalcites II	Experiment number: 26-01- 839
Beamline: SNBL	Date(s) of experiment: 18-23 June 2009	Date of report: 31-08-2009
Shifts: 15	Local contact(s): Olga Safonova (SNBL), Wim Bras (Dubble)	
Names and affiliations of applicants: Stéphane Walspurger, Paul Cobden, Gerard Elzinga, Ruud Westerwaal Wim Haije Energy Research Centre of the Netherlands, PO BOX 1 1755 ZG Petten, The Netherlands		

Background and strategy

Hydrotalcite (HT) materials $(M_x^{2+} M_{1-x}^{3+})(OH)_2(CO_3)_{1-x} \cdot yH_2O$, comprising Mg and Al, are currently being investigated as CO₂ sorbents for pre-combustion carbon capture in coal or natural gas 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 CO₂ on hydrotalcite and especially K₂CO₃ promoted HT needs to be thoroughly studied at relevant pressures and temperatures for further understanding and optimisation of sorbent materials. In situ high resolution XRD, XAS and Raman are tools of choice to get new insights on local coordination changes of Mg/Al during thermal decomposition and CO₂ ad/desorption cycles under 10bars comprising steam and/or CO₂ (high pressure experimental setup at SNBL). Furthermore, structural rearrangement of the material should bring useful information about the nature of adsorption sites and the role of alkali promoters. Experimental strategy has included the study of alkali promoted aluminas which are parent materials of alkali promoted HT and may bring insights on the requisite for optimal CO₂ sorbent properties.

Results obtained at ESRF in June 2009

Preliminary validation tests on SNBL high temperature/high pressure gas cell have been carried out in April 2009 to upgrade the cell with a reliable heat tracing as well as a new gluing procedure for capillary connections. Accordingly, the gas cell has been successfully tested for operation under 10 bar CO₂/steam (1:1) at temperature up to 600°C. Commercial alkali promoted HT has shown that MgCO₃ crystalline phase appears between 300-400°C under CO₂-steam (10 bar 1:1) conditions (Figure 1).



Importantly this experiment shows that HT structure has first been lost before MgCO₃ has been actually formed. Moreover it seems that Potassium interaction with alumina is sufficiently strong to generate crystalline Dawsonite-type of carbonate (KAlCO₃(OH)₂) observed at 200 and 300°C. A full cycle of adsorption (at 10 bars CO₂/steam) and desorption at 1 bar N₂ dry has further evidenced that the structural rearrangement from MgO to MgCO₃ is the bulk process occurring during the pressure swing adsorption process. Although being alumina based Mg-free materials, alkali promoted aluminas have also shown a great potential for CO₂ sorption in lab

scale experiments. We have thus carried out a similar XRD experiment on a commercial Potassium carbonate promoted alumina. Interestingly, the formation of K-Dawsonite ($\text{KAlCO}_3(\text{OH})_2$) was further confirmed at temperature below 400°C . At higher temperature, Dawsonite structure is lost and a new K-Mullite type crystalline phase $\text{K}_{0.67}\text{Al}_6\text{O}_{9.33}$ has been observed along with bulk crystalline Potassium carbonate phase at 400°C and above (Figure 2). While decreasing the temperature to 200°C , the reformation of K-Dawsonite crystalline phase has been evidenced. Together with other XRD experiments on K-Dawsonite, our results show that K^+ ions mobility within alumina lattice is greatly enhanced by the presence of both steam and CO_2 at high pressure. Confirming few previously reported data on alkali ion migration in alumina, it seems that fast hydroxylation-dehydroxylation of the alumina may enhance the insertion of $\text{K}_2\text{O}(\text{CO}_2)$ between the close packed layers of transitional alumina to provide bridging oxygens. Hence K^+ ions redistribute rather quickly in the alumina lattice and allow reversible formation of species such as K_2CO_3 , K-Dawsonite and K-Mullite. These results will be published in a short communication in Chemistry of Materials and further work is ongoing to understand what the impact of migration processes could be on reversible adsorption of CO_2 .

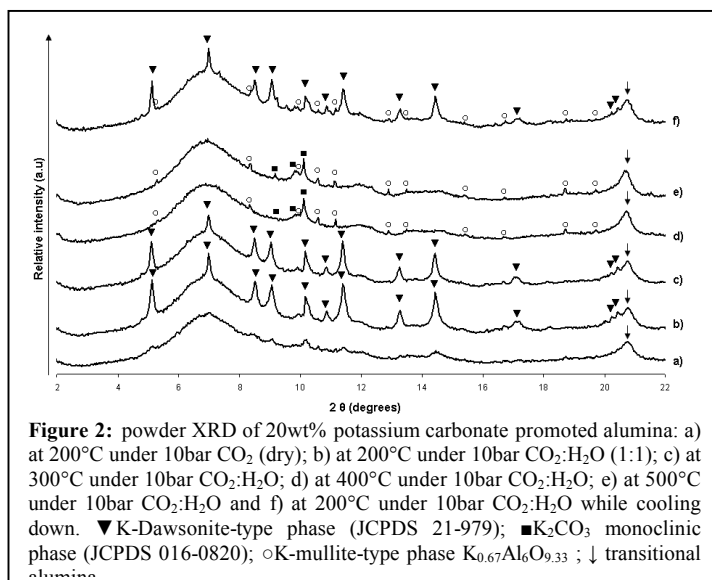


Figure 2: powder XRD of 20wt% potassium carbonate promoted alumina: a) at 200°C under 10bar CO_2 (dry); b) at 200°C under 10bar $\text{CO}_2:\text{H}_2\text{O}$ (1:1); c) at 300°C under 10bar $\text{CO}_2:\text{H}_2\text{O}$; d) at 400°C under 10bar $\text{CO}_2:\text{H}_2\text{O}$; e) at 500°C under 10bar $\text{CO}_2:\text{H}_2\text{O}$ and f) at 200°C under 10bar $\text{CO}_2:\text{H}_2\text{O}$ while cooling down. ▼ K-Dawsonite-type phase (JCPDS 21-979); ■ K_2CO_3 monoclinic phase (JCPDS 016-0820); ○ K-mullite-type phase $\text{K}_{0.67}\text{Al}_6\text{O}_{9.33}$; ↓ transitional alumina

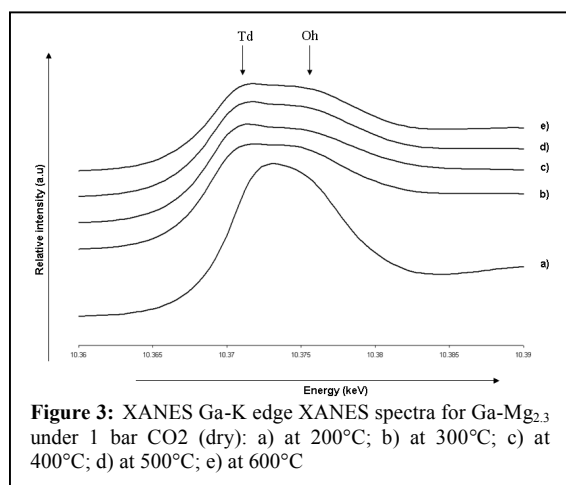


Figure 3: XANES Ga-K edge XANES spectra for $\text{Ga-Mg}_{2.3}$ under 1 bar CO_2 (dry): a) at 200°C ; b) at 300°C ; c) at 400°C ; d) at 500°C ; e) at 600°C

For XAS studies (according to the available energies in the beam at ESRF), Al atoms had been substituted by Ga and K by Rb. The first series of experiments have been carried out on Ga-Mg HT to confirm the influence of atomic substitution and rearrangement observed in the previous project 26-01-839 (June 2008). In addition to XRD experiments which have confirmed that the decomposition pathway is the same as purely Mg-Al HT, XAS studies performed at under 1 bar CO_2 have shed light on the rearrangement of Ga to both octahedral and tetragonal configurations upon the effect of heating (Figure 3).

The Ga environment changes dramatically with increased temperature from a mostly octahedral environment to a mixed tetrahedral/octahedral environment (XANES peak at 10.373 keV

and 10.378 keV respectively)[2], as found earlier [3] and attributed to the early stage of spinel (MgGa_2O_4) formation. These data will be further correlated with EXAFS results to get more insights about the rearrangement of Ga in HT. Moreover experiments on Rubidium carbonate promoted HT have shown decomposition and general behaviour very similar to what had been observed with the commercial Potassium promoted-HT material. EXAFS data at the Rb edge are under investigation and may bring further evidence in ions migration mechanism in layered double hydroxide.

Experimental setup

We have been able to implement and use high pressure gas cell without any condensation of steam by an optimisation of the cell insulation and connectivity during preliminary visit in April 2009. Due to a power shortage at the beginning of our shifts, Raman spectroscopy could not be used in this campaign. As a carbonate sensitive technique, Raman should have brought essential information about the fate of CO_2 in the material and the carbonate environment. SNBL gas cell configuration with simultaneous Raman, XAS and XRD under relevant pressure is a unique environment to acquire such useful information.

[1] B. Metz et al, IPCC report on carbon dioxide capture and storage (2005)

[2] K. Shimizu et al J. Phys. Chem. B 103 (1999), 1542

[3] J. A. Van Bokhoven et al Chem. Eur. J. 7 (2001), 1258.