



	<b>Experiment title:</b> <b>Hydrotalcites</b>	<b>Experiment number:</b> 26-01-790
<b>Beamline:</b> SNBL	<b>Date(s) of experiment:</b> 25-30 June 2008	<b>Date of report:</b> 12-09-2008
<b>Shifts:</b> 15	<b>Local contact(s):</b> Olga Safonova (SNBL), Wim Bras (Dubble)	
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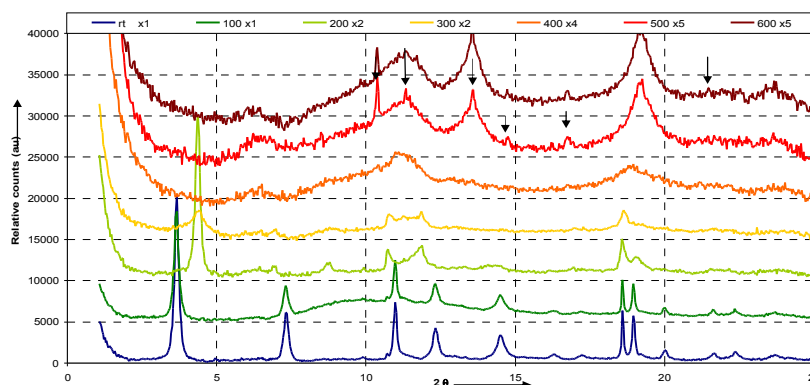
### Background and strategy

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 CO<sub>2</sub> sorbents for pre-combustion carbon capture in coal or natural gas fired power plants to reduce greenhouse gas emissions [1]. Although being used successfully in a sorption enhanced water gas shift bench scale unit at ECN, adsorption of CO<sub>2</sub> on hydrotalcite and especially K<sub>2</sub>CO<sub>3</sub> promoted HT is not yet fully understood, mostly because the characterization using conventional equipment is not trivial due to both the poor crystallinity and the heterogeneous nature of the products of the thermal decomposition steps as a function of temperature.

In situ high resolution XRD, XAS and Raman should yield information on local coordination changes of Mg/Al during thermal decomposition and CO<sub>2</sub> ad/desorption cycles at 670K under 10-20 bars comprising steam and/or CO<sub>2</sub> (high pressure experimental setup at SNBL). Furthermore, it should give insight in the nature of adsorption sites and role of alkali promoters.

### Results obtained at ESRF in June 2008

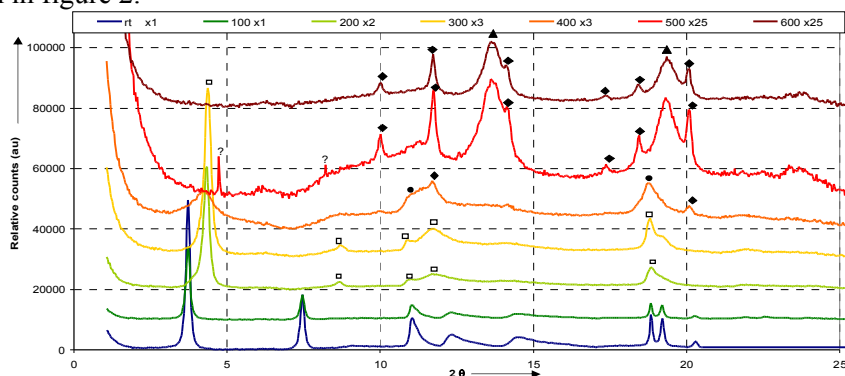
For XAS studies (according to the available energies in the beam at ESRF), Al atoms have been substituted by Ga. The first series of experiments have been carried out on pure Al-Mg<sub>1.8</sub>, pure Ga-Mg<sub>2.3</sub> and partial substituted Ga/Al-Mg<sub>1.8</sub> HT to check the influence of atomic substitution. Figure 1 shows the decomposition the pure Ga.Mg<sub>2.3</sub> HT as a function of temperature at 5 bars CO<sub>2</sub> pressure. In detail, the typical diffractogram of crystalline HT is observed for RT and 100°C. For 200 and 300°C the well known collapse of the interlayer is clearly observed. Remarkably, this phase is still present at 300°C under these conditions.



**Figure 1: XRD patterns of Ga-Mg<sub>2.3</sub> HT as a function of the temperature under 5 bars CO<sub>2</sub> pressure (the arrows indicate the formation of MgCO<sub>3</sub> crystalline phase).**

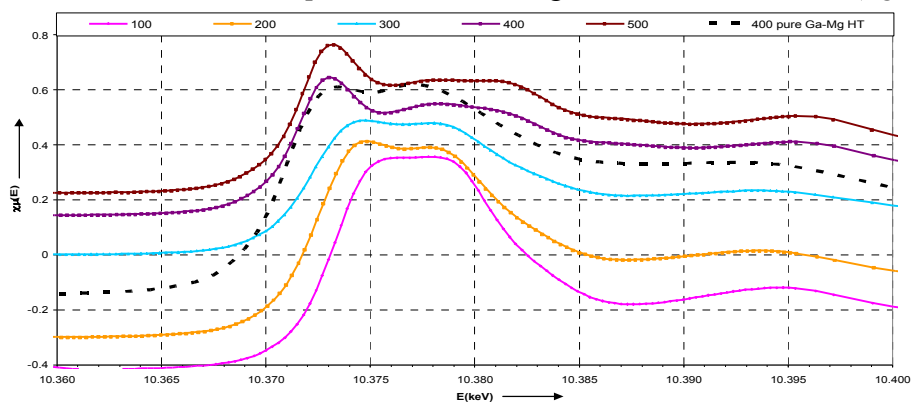
At 400°C, the collapse of HT phase seems to be completed and a new, yet unknown, phase appears with two broad diffraction peaks with weak intensity. At higher temperature, this intermediate phase still exists and crystalline MgCO<sub>3</sub>

and MgO phases are clearly observed. As confirmed by a supplementary experiment,  $\text{MgCO}_3$  starts decomposing at temperatures higher than  $400^\circ\text{C}$  under these conditions. Very similarly, the pure Al- $\text{Mg}_{1.8}$  HT (at 1 bar  $\text{CO}_2$  pressure) decomposed to an intermediate phase at  $400^\circ\text{C}$  which transformed to MgO at higher temperature. Note that at 1 bar  $\text{MgCO}_3$  crystalline phase could hardly be detected and that at 5 bars  $\text{CO}_2$  pressure its fingerprint is very well defined. In contrast, in 2 experiments with  $\text{Ga}_{0.25}\text{Al}_{0.75}\text{-Mg}_{1.8}$  at 1 and 5 bar  $\text{CO}_2$ , a completely different decomposition pathway has been observed as shown in figure 2.



**Figure 2: XRD patterns of  $\text{Ga}_{0.25}\text{Al}_{0.75}\text{-Mg}_{1.8}$  HT versus T at 1 bar  $\text{CO}_2$  (□ for the crystalline collapsed HT; ● intermediate phase; ◆ spinel  $\text{Mg}[\text{Al}(\text{Ga})]_2\text{O}_4$  and ▲ for MgO phase).**

Actually, below  $400^\circ\text{C}$ , the decomposition followed the same trend observed in previous experiments, but a spinel phase was formed at  $400^\circ\text{C}$  and increased crystallinity at higher temperature. Formation of crystalline spinel at such a low temperature is quite surprising and may most probably be the consequence of destabilisation of the structure involved by substituting only a fraction of Al for Ga. Note also that no  $\text{MgCO}_3$  could be detected in these experiments. XANES experiments have been carried out on pure  $\text{Ga}_{0.25}\text{Al}_{0.75}\text{-Mg}_{1.8}$  HT under 5 bars  $\text{CO}_2$  (figure 3).



**Figure 3: Ga-K edge XANES spectra for  $\text{Ga}_{0.25}\text{Al}_{0.75}\text{-Mg}_{1.8}$  HTC versus T (coloured lines) and for Ga- $\text{Mg}_{2.3}$  at  $400^\circ\text{C}$ , 5bars  $\text{CO}_2$  pressure (dashed line).**

The Ga environment changes dramatically with increased temperature from an octahedral environment (signal centred at 10.378 keV) to a mixed tetrahedral/octahedral environment (peak at 10.373 keV and 10.378 keV respectively)[4], as found earlier [5] and attributed to the early stage of spinel formation. It seems that XANES data confirm that substitution of only part of Al for Ga enhances some rearrangement of the structure. Interpretation of the EXAFS data is still in progress. Interestingly, an experiment under the same conditions with a fully substituted Ga- $\text{Mg}_{2.3}$  HT seems to show that less tetrahedral Ga is formed at  $400^\circ\text{C}$ . Further XRD experiments have been carried out on alkali promoted samples. Rubidium carbonate promoted HT have shown decomposition and general behaviour very similar to what had been observed with the fully substituted Ga-containing material. However EXAFS data at the Rb edge were not properly acquired so as to yield reliable data on the coordination of the Rb ion and its interaction with Al atoms.

### **Experimental setup**

Due to high fluorescence of HT and drift of the capillary with changing experimental T, Raman spectra had very poor quality. Sealing of the capillary was not sufficient to reach the desired pressures of 20 bar and the use of steam was hampered by condensation in different parts of the system, although tracing had been applied, inducing unwanted pressure drops. Our team and the local contacts agreed on scrutinizing options for an improved sample environment.

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