ESRF	**Experiment title: Formation and transformation of catalytically active materials using time resolved *in-situ* synchrotron X-ray powder diffraction.**	**Experiment number**: 01-02-270
Beamline: BM01A	**Date of experiment**: from: 19/6 2000 to: 23/6 2000	**Date of report**: 7/4 2001
Shifts: 9	**Local contact(s)**: Dr. Silvia Capelli	*Received at ESRF:*

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Report:

Hydrotalcite is a layered double hydroxide (LDH) which is found as a naturally occurring mineral, $Mg_6Al_2{\bullet}(OH)_{16}{\bullet}CO_3{\bullet}4H_2O$. The layers have a brucite structure with Mg and Al randomly distributed in the center of OH^- octahedra. Water molecules and carbonate anions are situated between the layers, the carbonate balancing the amount of Al.

Transition metal substituted magnesium oxide catalysts formed from hydrotalcite-like materials are of interest as catalysts for e.g. polymerisation and dehydrogenation reactions. The catalysts are prepared by calcining layered hydrotalcite-like materials forming a MgO phase. At higher temperatures spinel phases and MgO are formed. Reaction with water vapor at elevated temperatures results in transformation of the catalyst. The catalytical properties of these materials are very sensitive to both chemical composition and formation conditions. We have studied the calcination process and the reaction of calcined hydrotalcite with water and water vapor. An interesting feature of hydrotalcites is that they can be regenerated from the MgO phase; i.e. the calcination is reversible, at least to some extent. Above 400ºC the oxide is formed, and hydrotalcite can be regenerated from the oxide when it is in contact with water or water/carbonate. Millange, Walton and O'Hare studied regeneration of hydrotalcite using *in situ* XRD techniques [1]. Their results show a variation of regeneration time with regeneration temperature (25-120ºC).

To study regeneration of hydrotalcite in water at temperatures between 20 and 50ºC, we used a 0.9 mm quartz glass capillary in hot air stream [2,3]. Water was added to a capillary filled with oxide (hydrotalcite calcined at 400ºC). Series of diffractograms starting every minute was recorded at BM01A at ESRF using the MAR345 imaging plate system. Experiments were performed at 22, 30, 40, and 50ºC. The temperature was calibrated using the thermal expansion of silver metal.

Figure 1 shows a three dimensional plot of powder diffraction patterns collected during the reaction with water. Figure 2 shows the variation of regeneration time with temperature. It is observed that our method gives a shorter regeneration time than [1]. This might be due to the two different setups: we used a capillary and water, while Millange et al. [1] used an aqueous K_2CO_3 solution and a magnetic stirrer.
A continuation of these studies is in progress where the effect of varying the Mg/Al ratio will be investigated.

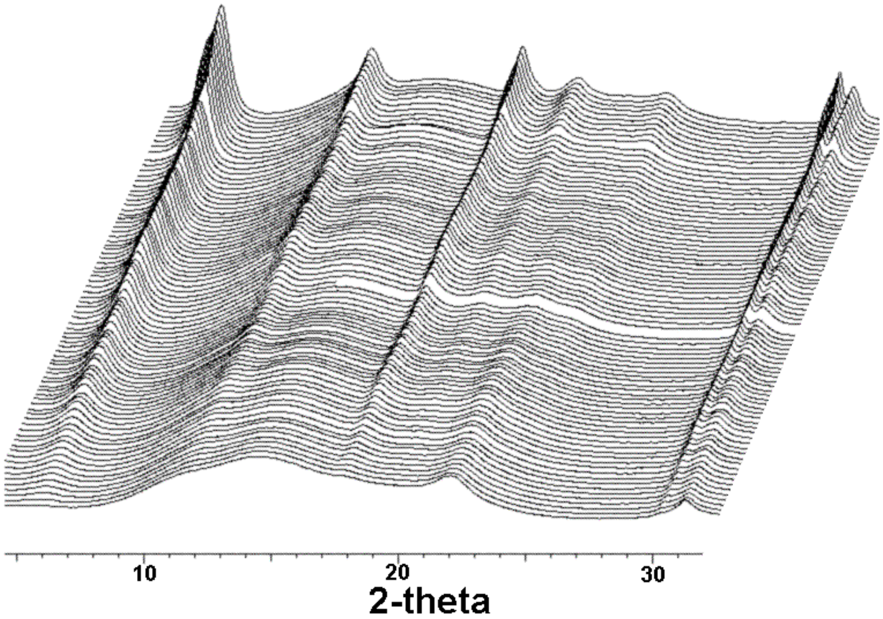

Figure 1. 3-Dimensional representation of a time resolved in-situ powder diffraction experiment showing the regeneration of hydrotalcite in water.

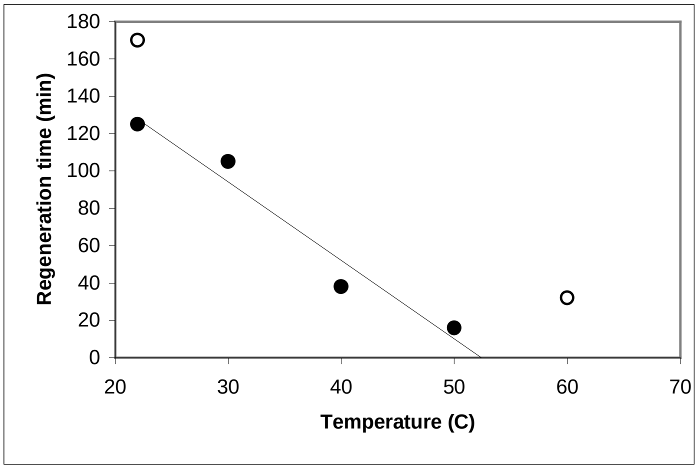

Figure 2. Regeneration time as a function of temperature, filled circles: this work; open circles from Millange, Walton and O'Hare [3].

References

1. **Millange, F.; Walton, R. I.; O'Hare, D**. *J. Mater. Chem.* 2000, *10*, 1713-1720. Time-resolved *in situ* X-ray diffraction study of the liquid-phase reconstruction of Mg-Al-carbonate hydrotalcite-like compounds.
2. **P. Norby**, "Synchrotron powder diffraction using Imaging Plates; Crystal structure determination and Rietveld refinement" *J. Appl. Cryst.* **30** (1997) 21-30.
3. **P. Norby**, "Hydrothermal Conversion of Zeolites: An *In-situ* Synchrotron X-ray Powder Diffraction Study" *J. Amer. Chem. Soc.* **119** (1997) 5215 -5221.