Microwave calcination of Cu/Mg/Al hydrotalcite catalyst precursor

H. E. Cross, G. Parkes and D. R. Brown*

Centre for Materials and Catalysis Research, Department of Chemical and Biological Sciences, University of Huddersfield, Huddersfield HD1 3DH, UK.

d.r.brown@hud.ac.uk
Tel 44 1484 473397 Fax 44 1484 472182

Keywords Catalyst; catalysis; calcination; microwave; feedback-control; hydrotalcite; layered double hydroxide; mixed metal oxides; calorimetry; solid base.

Abstract

A copper-substituted hydrotalcite ($Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$) has been subjected to calcination under feedback-controlled microwave heating, in which microwave power is continuously modulated to generate a defined sample temperature programme or constant sample temperature. The results show that microwave calcination results in enhanced crystallinity of the resultant oxides and spinel phase formed at high temperature, compared to conventional calcination. In addition, an additional phase, Cu_2MgO_3, is detected following microwave calcination, at a bulk temperature very much lower than previously reported for copper-containing hydrotalcite. The concentrations and strengths of surface basic sites are significantly higher for materials calcined using microwaves than using conventional heating. Catalytic activities in the base-catalysed transesterification of glyceryl tributyrate with methanol are also higher. We suggest that microwave calcination under feedback-control, while allowing control of material bulk temperature during calcination and preventing major temperature excursions, may allow quite large but highly localised temperature variation, for instance as water is released during dehydroxylation, which are beneficial in developing surface defects and surface basicity.

1. Introduction

Solid materials prepared using microwave heating can yield products that differ from those generated by conventional heating, in part because different processes are induced by microwaves and also because direct heating by microwaves occurs throughout the body of a solid sample and is not restricted to the solid surface [1-7]. This is particularly important where a thermally-induced transformation results in the release of gases or vapours which have to diffuse to the surface through material which may or may not have already reacted. In these cases, different morphologies might reasonably be expected, depending on reaction gradients established between bulk and surface sites. The different heating rates under microwave heating experienced locally by, for instance, water released in a solid state transformation may also influence the nature of the ultimate products.

Despite the potential for control of surface and other properties, microwave techniques are largely unexploited for solid state processes. This is mainly because the required control of the heating process can be difficult, especially when a solid material undergoes a transformation which is accompanied by a change in the way the material couples with a microwave field. We are able to overcome this problem by using feedback-controlled microwave heating, in which the microwave power is controlled through continuous feedback from measurement of sample temperature to the microwave generator [8].

Figure 1 illustrates the value of feedback-control in a typical microwave calcination (of a copper-containing hydrotalcite). Application of a linear increase in microwave power (Fig. 1a), as an example of a heating programme with no feedback-control, results in fluctuations in sample temperature and, most importantly, temperature runaway above 450 ^{o}C. In contrast, under feedback-control (Fig. 1b) the power is varied to maintain a defined sample temperature ramp, dropping rapidly when the sample temperature reaches just over 400 ^{o}C to prevent the temperature runaway seen with no feedback-control.

Figure 1

It is worth mentioning that feedback control of microwave power can also be based on the weight of the sample, adjusting power to maintain a constant rate of sample weight loss. Where a solid state reaction is taking place that involves weight loss, this method is equivalent to maintaining a constant rate of reaction through the programme. Control can also be exerted based on the partial pressure of an evolved gas [8-10].

Layered hydrotalcite-type mixed metal hydroxides, the best known of which is based on magnesium hydroxide in which some of the metal ions are isomorphously substituted by aluminium ions, yield intimate mixtures of the oxides of the metals on calcination. These materials tend to have relatively high surface areas and they frequently show high catalytic activities, most commonly as solid bases .[11-15] The basicity can be tuned and other catalytic properties can be imparted through the incorporation of a range of catalytically active, usually divalent, metals in the brucite lattice structure [15-20]. Conventional hydrotalcites tend to show little catalytic activity in their original form but calcination yields solid mixed oxides which are, most often, Lewis bases. Brönsted basicity can be generated in the original hydrotalcite by exchange of the interlayer carbonate ions for hydroxide ions [15]. The basic properties of hydrotalcites also result in their application as adsorbents for pollutants such as NO_x and SO_x [21-23].

The calcination of hydrotalcite by conventional methods has been studied in detail [24-26]. Progressive temperature increase results in the loss of physically bound water and water in the interlayer regions, followed by desorption of water coordinating exchangeable anions. If carbonate anions are present, they decompose above 300 ^{o}C, although it is thought that this process may not be absolutely complete until the calcination temperature reaches 700 ^{o}C or even 800 ^{o}C [26]. The last major process is the dehydroxylation of the crystalline matrix to generate the oxides, at 400-500 ^{o}C. This is characterised by the appearance of broad lines in the X-ray diffraction pattern associated with the oxides, indicative of small crystallites. Raising the temperature further results in sintering of the

oxides and the formation of spinel phases. This is usually associated with a reduction in solid base catalytic activity [16]. When transition metals are isomorphously substituted for magnesium or aluminium, additional processes can occur on calcination, including reduction of the oxides to the corresponding metals at high temperature [25, 27].

Conventional heating techniques under feedback-control have previously been applied to hydrotalcite-type materials [28,29]. This earlier work is significant in that it demonstrates how feedback-control methods can be used to effectively resolve the processes leading to the loss of loosely bound water, dehydroxylation of the lattice and decomposition of interlayer carbonate ions, in a way not normally possible. So far these techniques have not been applied to microwave calcination of hydrotalcites. There is some reported work on the use of microwaves for hydrotalcite calcination, but crucially it has been without precise temperature control [30]. And since hydrotalcite calcination involves major changes in the way the solid couples with microwaves (as water is lost), temperature runaway is possible. It has to be accepted that temperatures achieved with uncontrolled microwave heating are unpredictable. Looking more widely at microwave calcination processes, it is worth pointing out that other methods have been used to exert at least some control over the temperature of the solid. In the synthesis of ceramics for example, microwaves have frequently been used to induce solid state transformations using an inert support matrix to moderate temperature excursions [31], but it is important to note that this does not provide the level of control available through continuous feedback methods.

In the work reported here we have studied the effects of microwave calcination of copper-containing layered hydroxides on the structural and catalytic properties of the mixed metal oxides produced. The work is based on a layered metal hydroxide containing aluminium, magnesium and copper(II) ions. Microwave calcination has been carried out using an indigenously developed feedback-control system, based on a tuned microwave cavity in which the sample is held at the anti-node of the fundamental stationary wave, itself produced by a variable power supply controlled by feedback from a pyrometer continuously measuring the sample temperature. The mixed metal oxides produced using

this system have been characterised in terms of their crystallinities, their specific surface areas, their basicities (concentrations and strengths of basic sites measured by carbon dioxide adsorption calorimetry), and their catalytic activities. The model reaction used has been the base-catalysed transesterification of glyceryl tributyrate with methanol (Scheme 1). This reaction is a mimic for the transesterification of vegetable oils used in biodiesel synthesis. From the point of view of catalyst testing, the use of glyceryl tributyrate has an advantage over vegetable oils in that it is fully miscible with methanol, meaning that it is easier to ensure that the transesterification reaction is carried out in the regime of kinetic rather than diffusion control.

Scheme 1

2. Experimental

2.1. Catalyst preparation

All reagents were of Analar grade. Metal nitrates were purchased from Sigma-Aldrich. A layered double hydroxide based on magnesium and aluminium (with an M^{2+}/M^{3+} ratio of 3.0) in which half the magnesium(II) in the synthesis mixture is substituted by copper(II) was prepared by adding slowly a 250 mL solution of magnesium, copper and aluminium nitrates, (total concentration 1.00 mol dm^{-3}), to a 250 mL solution of sodium carbonate, (0.625 mol dm^{-3}) with stirring. The pH of the solution was maintained at 8-9 using sodium hydroxide solution (0.0200 mol dm^{-3}). The resulting mixture was aged at 65 ^{o}C for two hours, cooled and filtered. The precipitate was washed thoroughly and dried at 100 °C overnight.

Powders, as 2.0 g samples, were calcined both conventionally in a muffle furnace in flowing dry air, and under feedback-controlled microwave heating at temperatures from 400 °C to 750 °C in flowing dry air, by heating at 2 °C min^{-1} and then holding at the calcination temperature for four hours. All measurements refer to the calcined materials. Calcined samples were transferred to the reaction mixture in a desiccator.

2.2. *Microwave calcination*

Samples were calcined in the microwave field in a single mode tuned cavity, using feedback-control to maintain the temperature ramp and a constant temperature in the isothermal region. In this system a variable power (to 1 kW) Industrial Microwave Systems microwave generator operating at 2.45 GHz through a Remote Head, feeds a wave guide with a three stub tuner. A resonant cavity accommodates the sample, positioned on a silica stub. The sample can be in the form of a pressed disc (or discs) or as a powder held in a silica crucible. The sample stub and sample are in a vertical silica sleeve through which a flow (5 mL min^{-1}) of dry air is maintained. Sample temperature is monitored using an Omega Engineering infrared pyrometer located a minimum distance above the sample cavity. The power is controlled using algorithms designed so that the sample follows a defined temperature, sample mass or evolved gas programme [8-10]. In the work reported here feedback was controlled to maintain a sample heating rate of 2 ^{o}C min^{-1}, followed by an isothermal stage.

2.3. *Catalyst characterisation*

2.3.1. *XRD, N_2 adsorption and XPS*

Catalysts were stored in a dry atmosphere at room temperature. They were characterised by powder X-ray diffraction using Cu Kα radiation (Bruker AXS-D8 Advance Diffractometer) and by nitrogen adsorption at -196 °C (Micrometrics ASAP 2020) after degassing at 150 °C, using 30 data points. Surface areas were determined from adsorption isotherms (BET). Exposure to air for oxide samples was minimised to prevent reaction with water vapour and conversion back to hydroxides. The close-to-surface elemental composition of the copper-substituted hydrotalcite was determined by X-ray photoelectron spectroscopy, at the Institut de Recherches sur la Catalyse et l'Environnment de Lyon.

2.3.2 *Calorimetric adsorption experiments*

Catalyst basicity was characterised by carbon dioxide adsorption calorimetry, under flow conditions, using a system based on a flow-through Setaram 111 differential scanning calorimeter (DSC) and an automated gas flow and switching system, with a mass spectrometer connected via a heated capillary (at 175 °C) for the down-stream gas flow detection [32,33]. In a typical experiment a sample (~50

mg) is activated under dry nitrogen (5 mL min^{-1}) for one hour at 200 °C. It is then cooled to 120 °C and small pulses (typically 1 mL) of the probe gas (1% carbon dioxide in nitrogen) are injected at regular intervals into the carrier gas stream from a gas sampling valve. The concentration of carbon dioxide (m/z – 44) downstream of the sample is monitored. An important feature of the flow calorimetric technique is that net heat measurements relate only to carbon dioxide bound irreversibly to the samples. Reversibly bound carbon dioxide desorbs when the gas flow reverts to the carrier gas. The net amount of carbon dioxide irreversibly adsorbed from each pulse is determined by comparing the mass spectrometer signal during each pulse with a signal recorded during a control experiment through an empty sample tube. Net heat released for each pulse is calculated from the DSC thermal curve. From this the molar enthalpy of adsorption (ΔH^{o}_{ads}) is obtained for the carbon dioxide adsorbed from each pulse. In this work, each sample was analysed in triplicate under the same experimental conditions. Data is plotted as a profile of $\Delta H^{o}_{ads}(CO_2)$ vs. amount of carbon dioxide irreversibly adsorbed.

2.4 Catalytic activities

The catalytic activities of the oxides were determined in the transesterification of glyceryl tributyrate (tributyrin) with methanol. Methanol (12.0 mL, Sigma-Aldrich, purity 99.8%), internal standard dihexyl ether (0.5 mL, Sigma-Aldrich) and glyceryl tributyrate (5.0 mL, Sigma-Aldrich, purity ≥99%) were placed in a 50 mL three-necked round bottom flask with a condenser attached, and heated with stirring at 250 rpm, to 65 °C. The catalyst (250 mg) was activated at 150 °C for one hour prior to reaction and then added to the pre-heated reaction mixture. Conversion of tributyrin and product formation were monitored by GC, using a 25 m BP1 column at 1.4 mL min^{-1} helium flow, split ratio 28:1, at time zero and at regular intervals over a reaction period of three hours. Reaction rates were measured over a range of stirrer speeds to ensure that we were not operating in a diffusion control regime. Similarly, metal oxide powders were ground with a pestle and mortar under dry air and the reactions run again, to ensure that catalyst particle size was not affecting reaction rate. The possibility of catalyst leaching was eliminated by removing catalyst at an intermediate reactant conversion and confirming that the reaction ceased.

3. Results and Discussion

3.1 Copper-containing hydrotalcite

Elemental analysis by XPS indicated that the stoichiometry of the mixed hydroxide on which this study was based corresponded to $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$. Analysis by XPS is limited to regions close to the solid surface but there is no reason to suppose that the bulk composition would be significantly different. The powder X-ray diffraction pattern is shown in Figure 2 and is typical for a hydrotalcite-type material [15, 34, 35] and is not significantly different from the pattern detected by Kovanda et al. for a hydrotalcite with metal stoichiometry $Cu_2Mg_2Al_2$[36]. The unit cell parameters were obtained based on a 3R stacking sequence so the spacing d_{110} can be used to calculate the *a* unit cell parameter ($a = 2d_{110}$) which is sensitive to the ionic radii of the metal ions in the structure. Magnesium(II) and copper(II) ions have very similar radii so we cannot reasonably expect to be able to confirm the presence of copper(II) from this, but the value for *a* of 0.306 nm is broadly consistent with the composition, particularly the aluminium content, of the material [16]. The *c* parameter ($c = 3d_{003}$) is 2.33 nm for $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$. The value of this spacing is sensitive to the level of hydration but in this case is generally consistent with values detected for similar materials [16].

Figure 2

3.2 Calcination conditions and effects on catalyst properties

3.2.1 Products of calcination

The material was calcined in a conventional furnace and in the microwave cavity under temperature feedback-control to final temperatures up to 750 °C. Diffraction patterns recorded after calcination at 400, 500 and 750 °C are shown in Figure 3. Specific surface areas by nitrogen adsorption are shown in Table 1. Catalytic activities are also shown in the Table, in terms of the % conversions of glyceryl butyrate after 150 minutes reaction time. Conversion of glyceryl butyrate was monitored throughout

the reaction in all cases and the measured rates were essentially first order in this reactant (methanol was in large excess).

Figure 3

Figure 3 shows that, on calcination using both methods of heating, the material loses the hydrotalcite structure, and broad overlapping reflections due to MgO [37] and CuO [38] appear. As the temperature is increased further, the CuO reflections abruptly sharpen, clearly seen in the XRD pattern taken after microwave heating to 500 ^{o}C, followed by a similar sudden reduction in peak width for MgO, visible in the 750 ^{o}C microwave pattern but detected first at 550 ^{o}C (this XRD pattern is not shown). As heating continues reflections assigned to spinel, $MgAl_2O_4$ [39], appear under both types of heating. In fact, these could be due to a copper-containing spinel [25], the diffraction pattern for which may be indistinguishable from that of $MgAl_2O_4$.

The diffraction patterns of MgO and CuO sharpen very abruptly during the heating process, implying that sintering of the small oxide crystallites responsible for the broad line patterns occurs quite suddenly. In general, material heated using microwaves exhibits more intense and better resolved lines for CuO, MgO and for spinel, suggesting that greater crystallinity is achieved using microwave heating. Furthermore, the appearance of these phases occurs at nominally slightly lower temperatures under microwave heating, clearly seen by comparing XRD patterns taken after heating to 500 ^{o}C under the two heating regimes.

Figure 4

At higher temperatures, illustrated by the results at 750 ^{o}C in Figure 3, the spinel phase is clearly visible, but an additional phase is also seen at this temperature when microwaves are used. Reflections in the 750 ^{o}C microwave diffraction pattern are assigned in Figure 4 and the reflections associated with this new phase can be matched to those of Cu_2MgO_3, gueggonite, which has been

detected by others on heating simple solid mixtures of CuO and MgO in a conventional furnace to 1000 °C [40]. It has also been detected by X-ray diffraction in a copper-containing hydrotalcite of nominal stoichiometry $Cu_2Mg_2Al_2(CO_3)(OH)_{12}$ following calcination at 1000 °C, with reflections becoming quite intense at 1100 °C [36]. While we detected this phase at 750 °C under microwave heating, we could find no evidence for it when $Cu_{1.5}Mg_{4.5}Al_2(CO_3)(OH)_{16}.4H_2O$ was calcined under conventional heating, even to 1100 °C , despite the existence of a CuO/MgO mixture at temperatures above 500 °C. The relatively low copper content of the materials we have worked with is probably responsible for the absence of evidence for Cu_2MgO_3 on conventional calcination. The contrasting clear detection of Cu_2MgO_3 diffraction lines on microwave heating suggests the phase is formed relatively easily under this form of heating. Why this difference should exist is unclear but it does suggest that the processes induced by microwave heating are not the same as by conventional heating.

Table 1

There are small differences in the way the specific surface areas of the calcined materials change with calcination temperature, shown in Table 1. It is significant that specific surface areas go through maxima under both heating regimes, with materials calcined at 750 °C showing relatively low surface areas. Catalytic activities, on the other hand, increase with calcination temperature right through to 750 °C. Significantly, microwave calcined oxides show consistently higher activities than their conventionally calcined counterparts, despite the fact that their surface areas are generally lower. Analysis of the products of the transesterification show that selectivity to methyl butanoate at 2.5 hours reaction time is between 55 and 70%, and the patterns of selectivity are the same for the catalysts prepared in the two ways. The other products are the intermediate diglyceride and monoglyceride, and in all cases these are converted to the methyl ester completely as the reaction proceeds. The measured selectivities are consistent with the findings of other workers who used other calcined layered double hydroxide catalysts for the same reaction [12].

3.2.2 Catalyst basicities

Calorimetric CO_2 adsorption data for material calcined at 400, 500 and 750 ^{o}C is shown in Figure 5, in which $\Delta H^{o}_{ads}(CO_2)$ is plotted against the amount of CO_2 adsorbed by the sample. Catalyst basicities can be compared using these profiles, taking note of the extent of irreversible CO_2 adsorption with enthalpies greater than an arbitrary threshold of 60 kJ mol^{-1}, below which adsorption can reasonably be considered to be on sites of insignificantly low base strength. Other workers have used similar thresholds for this [11]. The molar enthalpies of CO_2 adsorption reflect the strengths of basic sites on which the probe gas is adsorbed, so the profiles shown in Figure 5 can loosely be interpreted in terms of basic site strength distribution profiles.

Figure 5

The profiles exhibited by mixed oxides generated by the two methods of heating are very different. Conventionally calcined materials at 400 and 500 ^{o}C show relatively few basic sites and relatively low base strengths (the first pulses of CO_2 adsorb at only 100-110 kJ mol^{-1}). The oxide produced at 750 ^{o}C shows stronger sites; the first pulse adsorbs at 133 kJ mol^{-1}. This material exhibits a higher concentration of basic sites at ca. 0.06 mmol g^{-1} based on the 60 kJ mol^{-1} cut-off, In contrast, the oxides produced by microwave calcination at 400, 500 and 750 ^{o}C show relatively strong base sites, with a significant part of the profiles in Figure 5b being above 120 k mol^{-1}. The concentrations of basic sites on these materials are much higher at 0.13-0.15 mmol g^{-1}, and the concentrations change relatively little over the calcination temperature range. It appears that surface basicity is generated by microwave heating much more effectively and at considerably lower temperatures than by conventional heating, both in terms of the concentrations of sites and site strengths.

Overall, the results show that there are significant differences between the products of calcination under the two modes of heating. The relative rates at which CuO and MgO are formed under microwave heating and the rates of subsequent conversions to spinel are significantly different to those observed under conventional heating, and material prepared using microwaves are more crystalline and have somewhat lower surface areas than materials calcined conventionally. In

addition, microwave heating appears to facilitate the formation of the additional phase, Cu_2MgO_3. Catalysts prepared using microwaves show higher surface basicities (concentrations and strengths of basic sites) and, consistent with this, higher catalytic activities in a base-catalysed reaction, although. differences in catalytic activities are not as great as might be expected based on CO_2 calorimetric adsorption data. In fact, catalysts calcined at 400 ^{o}C by both methods of heating show similar activities, despite the dramatic differences in both the concentration and strength of basic sites measured calorimetrically. At the two higher calcination temperatures, microwave-calcined catalysts are significantly more active, but these differences do not appear to correlate directly with either the abundance or the strength of basic sites. Values for base site turnover frequencies (TOF) would have been useful in explaining differences in catalytic activities but, because we have used a rather arbitrary threshold of CO_2 molar adsorption enthalpy on which to base our estimates of relative base site concentrations, we cannot calculate TOF values with any reliability. It seems likely to us that other factors, particularly pore structure and pore size, influence catalytic activity and, overall, it is not surprising that surface basicity alone is not a very good predictor of activity.

Some of these differences between catalysts prepared in the two ways may be linked to the different temperature gradients developed in solid samples as they are heated in a microwave field, and the relative rates at which dehydration, dehydroxylation and decarbonation occur in the bulk and near the surface of the solid. It is not unreasonable to suppose that the structural disruption, and the different water vapour pressures and CO_2 partial pressures to which regions of the sample would be exposed, could affect the conversion of one phase to another as the temperature is increased. However, the way in which surface basicity is developed so effectively under microwave heating suggests that this form of heating somehow facilitates the dehydroxylation step that generates the basic sites. It is possible that, as dehydroxylation occurs, the water released by the process is more susceptible to microwave heating than the rest of the solid. In this way, highly localised temperature excursions which are not affecting the bulk temperature significantly might occur, and it is possible that these high temperatures around the sites of oxide formation give rise to, firstly, highly effective

dehydroxylation and, secondly, the formation of surface defects and surface basicity as a consequence of very high local reaction rates.

The idea that microwave heating might produce highly localised hot spots, possibly as water is released from the lattice, might also explain the formation of Cu_2MgO_3. We suggest that the reason we do not detect this phase under conventional heating is that the copper content of the hydrotalcite we have worked with is relatively low and , even at 1100 ^oC, aggregation of sufficient copper ions to form detectable levels of Cu_2MgO_3 is not possible. But when microwave heating is employed, localised temperatures far is excess of this may be developed, facilitating aggregation and the formation of easily detectable levels of Cu_2MgO_3.

We suggest that microwave-induced processes, even when under control at a bulk sample level, may produce very large temperature differences within a solid material at a highly localised level.
If this is the case, and if temperatures far in excess of the bulk temperature are being experienced locally, then processes that would not normally be considered possible may need to be taken into account. In the case of hydrotalcites, the decomposition of carbonate ions is, in general, considered to be almost complete below 400 ^oC, but in fact it is known that complete decarbonation requires much higher temperatures, up to 800 ^oC [26]. There is infrared spectral evidence for a small proportion of the carbonate ions in the interlayer region becoming chemically grafted to the layered hydroxide, and it is likely that it is these grafted carbonate ions that decompose only at high temperatures [41]. It is conceivable that these grafted, thermally stable, carbonate ions remain intact on conventional calcination but are decomposed on microwave heating. And a possibility is that it is the complete removal of these interlayer carbonate ions that is required in order to generate the mixed metal oxides with maximised surface basicity.

To understand this further, it will be helpful to study hydrotalcites with other metals substituted for magnesium. Copper-containing hydrotalcites are generally thought to show lower basicities than hydrotalcites containing many other substituent metals, including lanthanum [42] and nickel [43], and

current work is directed towards hydrotalcites containing these other metals, with the objective of identifying the role of the transition metal substituent in the development of basicity under different modes of calcination.

4. Conclusion

The concentrations and strengths of basic sites on calcined $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$ are significantly higher when the hydrotalcite is calcined using microwaves, under feedback-control, than when using conventional heating. As would be predicted, this translates into higher catalytic activity in a base-catalysed reaction. It seems likely that, even when the microwave heating process is controlled via the bulk temperature of the solid, very high localised temperatures might be responsible for the formation of high concentrations of relatively strong basic surface sites.

We therefore believe that this work illustrates the value of feedback-controlled microwave heating for the conversion of hydroxides to metal oxid catalysts. The control ensures that bulk temperature runaway does not occur but, at the same time, allows for the sometimes beneficial local temperature excursions brought about by microwaves which can lead to increased surface basicity and catalytic activity.

4. Acknowledgements

The University of Huddersfield is thanked for a studentship (HEC). Thanks are due to Professor A Auroux of the Institut de Recherches sur la Catalyse et l'Environnment de Lyon (IRCELYON) for providing XPS measurements.

5. References

[1] A. Harrison, R. Ibberson, G. Robb, G. Whittaker, C. Wilson, I.D. Youngson, Faraday Discuss. 122 (2002) 363-399.

[2] D.R. Baghurst, R.C.B. Copley, H. Fleischer, D.M.P. Mingos, G.O. Kyd, L.J. Yellowlees, A.J. Welch, T.R. Spalding, D. O'Connell, J Organomet. Chem. 447 (1993) C14-C17.

[3] A.G. Whittaker, A. Harrison, G.S. Oakley, I.D. Youngson, S. King, R. Heenan, Rev. Sci. Instrum. 72 (2001) 172-176.

[4] M. Willert-Porada, Ceram. Trans. 80 (1997) 153-163.

[5] J.H. Booske, R.F. Cooper, I. Dobson, J. Mater. Res. 7 (1992) 495-501.

[6] J.H. Booske, R.F. Cooper, S.A. Freeman, K.I. Rybakov, V.E. Semenov, Phys. Plasmas, 5 (1998) 1664-1670.

[7] S.A. Freeman, J.H. Booske, R.F. Cooper, J. Appl. Phys. 83 (1998) 5761-5772.

[8] E.A. Fesenko, P.A. Barnes, G.M.B. Parkes, in: Sample Controlled Thermal Analysis. Hot Topics in Thermal Analysis and Calorimetry, 3 (Eds: O.T. Sorensen, J. Rouquerol) Springer: New York, 2004, pp.174-225.

[9] P.A. Barnes, E.L. Charsley, G.M.B. Parkes, Eur. Pharm. Rev. 11 (2006) 83-98.

[10] B.K.N.S. Kumar, G.M.B. Parkes, P.A. Barnes, M.J.N. Sibley, G. Bond, G. Rev. Sci. Instrum. 77 (2006) 045108/1-145108/9.

[11] H.A. Prescott, Z-L. Li, E. Kemnitz, A. Trunschke, J. Deutsch, H. Lieske, A. Auroux, J. Catal. 234 (2005) 119-130.

[12] J.L. Shumaker, C. Crofcheck, S.A. Tackett, E. Santillan-Jimenez, T. Morgan, Y. Ji, M. Crocker, T.J. Toops, Appl. Catal. B 82 (2008) 120-130.

[13] J.S. Valente, F. Figueras, M. Gravelle, P. Kumbhar, J. Lopez, J-P. Besse, J. Catal. 189 (2000) 370-381.

[14] D.G. Cantrell, L.J. Gillie, A.F. Lee, K. Wilson, Appl. Catal. A 287 (2005) 183-190.

[15] F. Figueras, Topics in Catal. 29 (2004) 189-196.

[16] J.S. Valente, J. Hernandez-Cortez, M.S. Cantu, G. Ferrat, E. Lopez-Salinas, Catal. Today 150 (2010) 340-345.

[17] I-C. Marcu, D. Tichit, F. Fajula, N. Tanchoux, Catal. Today 147 (2009) 231-238.

[18] D. Meloni, R. Monaci, V. Solinas, A. Auroux, E. Dimitriu, Appl. Catal. A 350 (2008) 86-95.

[19] L. Dussault, J.C. Dupin, E. Dumitriu, A. Auroux, C. Guimon, Surface & Interface Anal. 38 (2006) 234-237.

[20] A. Venugopal, J. Palgunadi, J-K. Deog, O-S. Joo, C-H. Shin, Catal. Today 147 (2009) 94-99.

[21] J.J. Yu, J. Cheng, C.Y. Ma, H.L. Wang, H.D. Li, Z.P. Hao, Z.P. Xu, J. Colloid and Interface Sci. 333 (2009) 423-430.

[22] M. Sanchez-Cantu, L.M. Perez-Diaz, A.M. Maubert, J.S. Valente, Catal. Today 150 (2010) 332-339.

[23] W. Zhongpeng, J. Zhi, S. Wenfeng, Catal. Commun. 8 (2007) 1659-1664.

[24] M.J. Hudson, S. Carlino, D.C. Apperley, J. Mater. Chem. 5 (1995) 323-329.

[25] S. Kannan, V. Rives, H. Knozinger, J. Solid State Chem. 117 (2004) 319-331.

[26] J.T. Kloprogge, L. Hickey, R.L. Frost, Appl. Clay Sci. 18 (2001) 37-49.

[27] R. Trujillano, M.J. Holgado, V. Rives, Solid State Science 11 (2009) 688-693.

[28] V. Vagvolgyi, A. Locke, M. Hales, J. Kristof, R.L. Frost, E. Horvath, W.N. Martens, Thermochim. Acta 468 (2008) 81-86.

[29] V. Vagvolgyi, S.J. Palmer, J. Kristof, R.L. Frost, E. Horvath, J. Colloid and Interface Sci. 318 (2008) 302-308.

[30] M.M. Amini, L. Torkian, Mater. Lett. 57 (2002) 639-642.

[31] M. Willert-Porada, T. Krummel, B. Rhohde, D. Moorman, Mater. Res. Soc. Symp. Proc. 269 (1992) 199-206.

[32] N.R. Shiju, H.M. Williams, D.R. Brown, Appl. Catal. B 90 (2009) 451-457.

[33] P.F. Siril, N.R. Shiju, D.R. Brown, K. Wilson, Appl. Catal. A 364 (2009) 95-100.

[34] J. Shen, J.M. Kobe, Y. Chen, J.A. Dumesic, Langmuir 10 (1994) 3902-3908.

[35] J. Rocha, M. del Arco, M.A. Ulibarri, J. Mater. Chem. 9 (1999) 2499-2503.

[36] F. Kovanda, K. Jiratova, J. Rymes, D. Kolousek, Appl. Clay Sci. 18 (2001) 71-80.

[37] JCPDS Card 4-829 Intl. Centre for Diffraction Data 1987.

[38] H. Wang, J-Z Xu, J-J Zhu, H-Y Chen, J. Crystal Growth 244 (2002) 88-94.

[39] JCPDS Card 21-1152 Intl. Centre for Diffraction Data 1987.

[40] H.G. El-Shobaky, J. Therm. Anal & Calor. 85 (2006) 32-327.

[41] T. Stanimirova, I. Veriglov, G. Kirov, N. Petrova, J. Mater. Sci. 34 (1999) 4153-4161.

[42] B. Veldurihy, J-M. Clacens, F. Figueras, J. Catal. 229 (2005) 237-242.

[43] C. Casenave, H. Martinez, C. Guimon, A. Auroux, A. Cordoneanu, E. Dumitriu, Thermochim Acta 379 (2001) 85-93.

Figure captions

Fig. 1. Temperature and power vs time plots for a copper(II)-containing hydrotalcite under microwave heating, a) where microwave power is increased linearly with time, showing sample temperature fluctuations and temperature runaway, and b) where the power is controlled to give a linear temperature increase.

Fig. 2. Powder XRD pattern of $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$.

Fig. 3. Powder X-ray diffraction patterns for $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$ following: a) conventional and b) microwave calcination, to the temperatures indicated.

Fig. 4. Powder X-ray diffraction pattern for $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$ following calcinations under microwave heating at 750 ^{o}C.

Fig. 5. Differential molar enthalpies of CO_2 adsorption vs. amount of CO_2 adsorbed at 120 ^{o}C for $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$ following calcination at 400, 500 and 750 ^{o}C under a) conventional and b) microwave heating.

Table caption

Table 1. Specific surface areas (BET) and catalytic activities of $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$ following conventional (furnace) calcination and feedback-controlled microwave calcination.

Table 1

Specific surface areas (BET) and catalytic activities of $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$ following conventional (furnace) calcination and feedback-controlled microwave calcination.

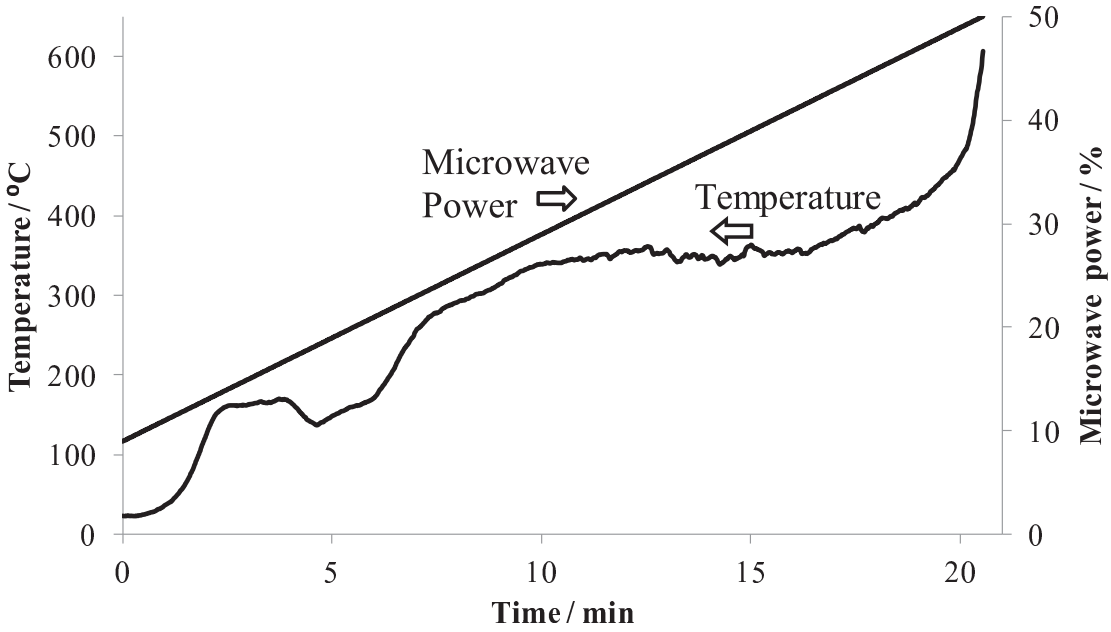
	Conventional heating			**Controlled microwave heating**		
Calcination temperature /°C	Surface area /m^2g^{-1}	Catalytic activity[a,b,c] /conversion of tributyrin after 2.5 hours /%	Product selectivity to methyl butanoate[d] /%	Surface area /m^2g^{-1}	Catalytic activity[a,b,c] conversion of tributyrin after 2.5 hours /%	Product selectivity to methyl butanoate[d] /%
-	60	0	-	60	0	-
400	88	20	55	86	21	58
500	101	26	61	84	34	64
750	59	33	63	21	46	68

[a] Methanol 12.0 mL; glyceryl butyrate 5.0 mL; catalyst 250 mg; reaction temperature 65 °C.
[b] Conversion vs. time data appears in Supplementary Data (ESI).
[c] 95% confidence limits = ±3%.
[d] 95% confidence limits = ±5%.

Figure 1

FIGURE 1

a)



b)

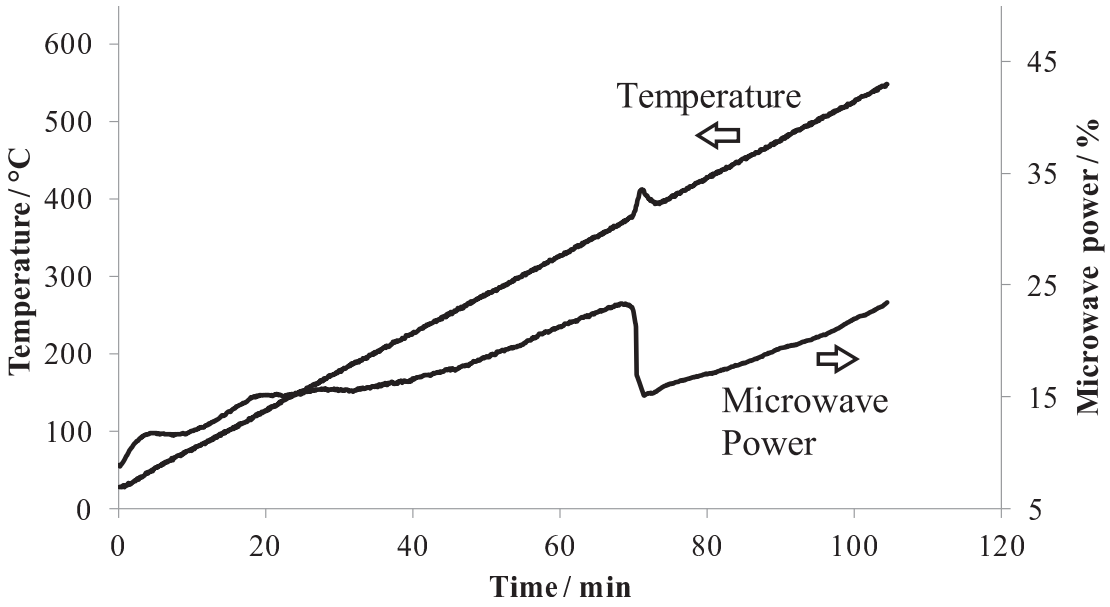


Fig. 1. Temperature and power vs time plots for a copper(II)-containing hydrotalcite under microwave heating, a) where microwave power is increased linearly with time, showing sample temperature fluctuations and temperature runaway, and b) where the power is controlled to give a linear temperature increase.

Scheme 1

SCHEME 1

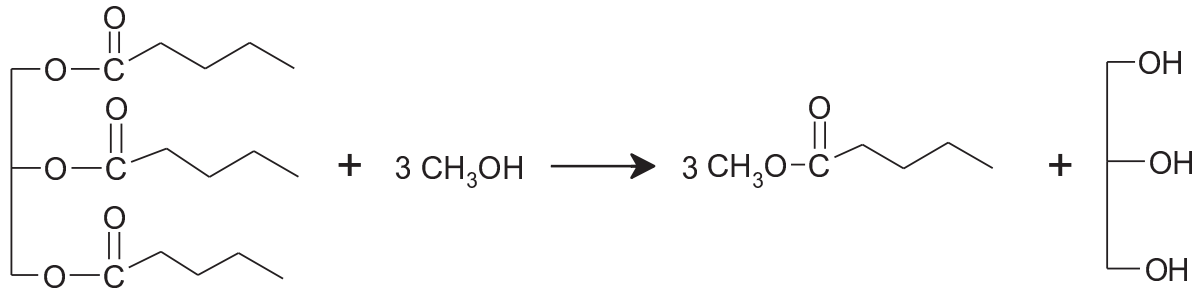


FIGURE 2

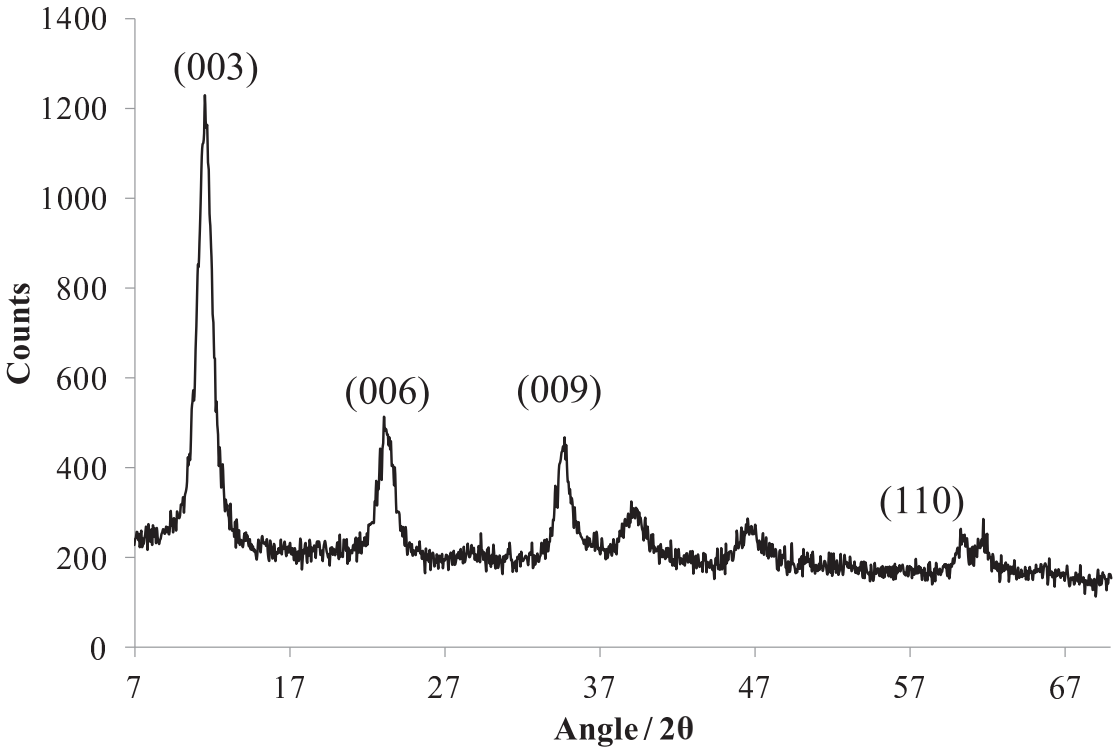


Fig. 2. Powder XRD pattern of $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$.

FIGURE 3

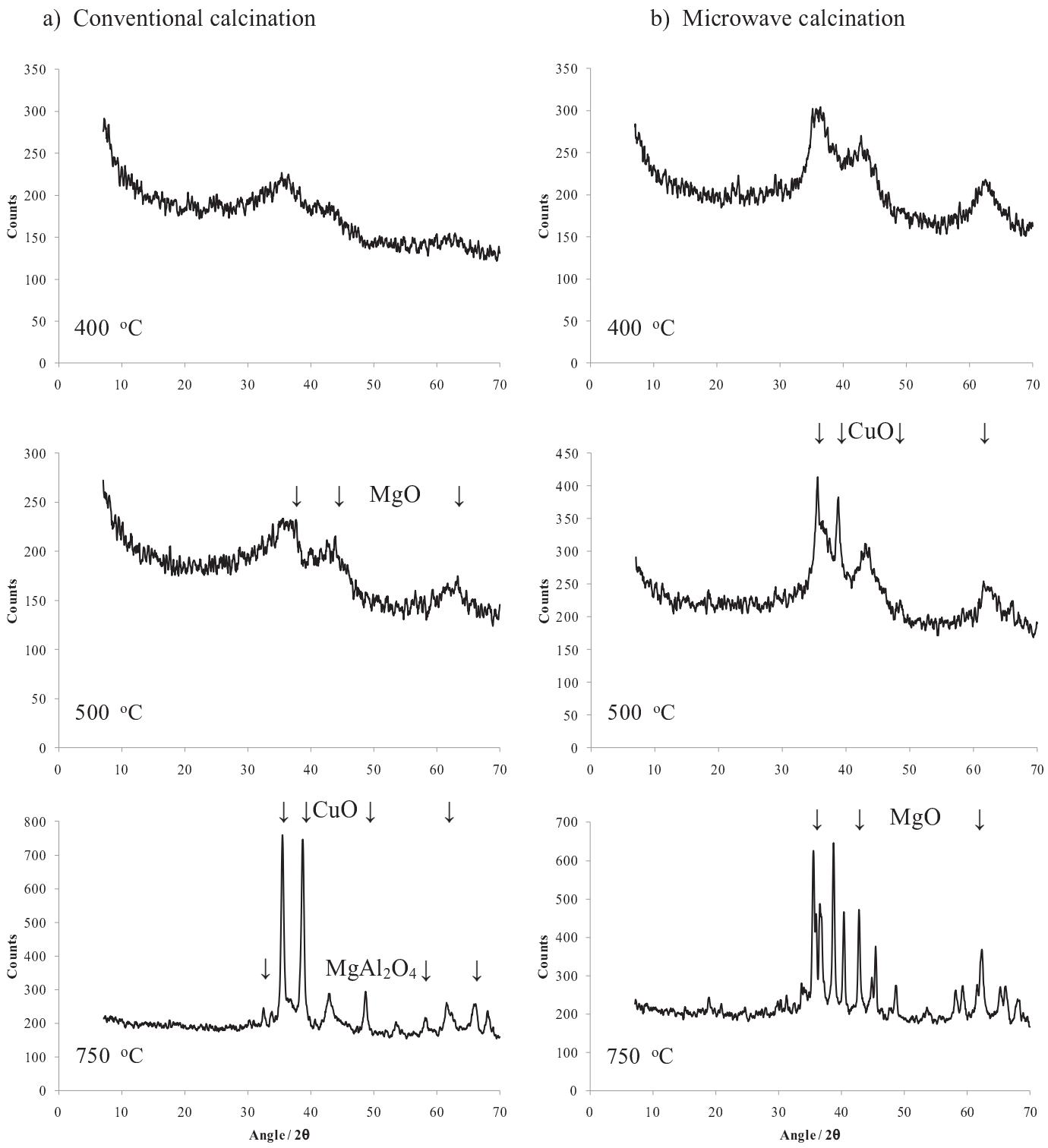


Fig. 3. Powder X-ray diffraction patterns for $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$ following: a) conventional and b) microwave calcination, to the temperatures indicated.

FIGURE 4

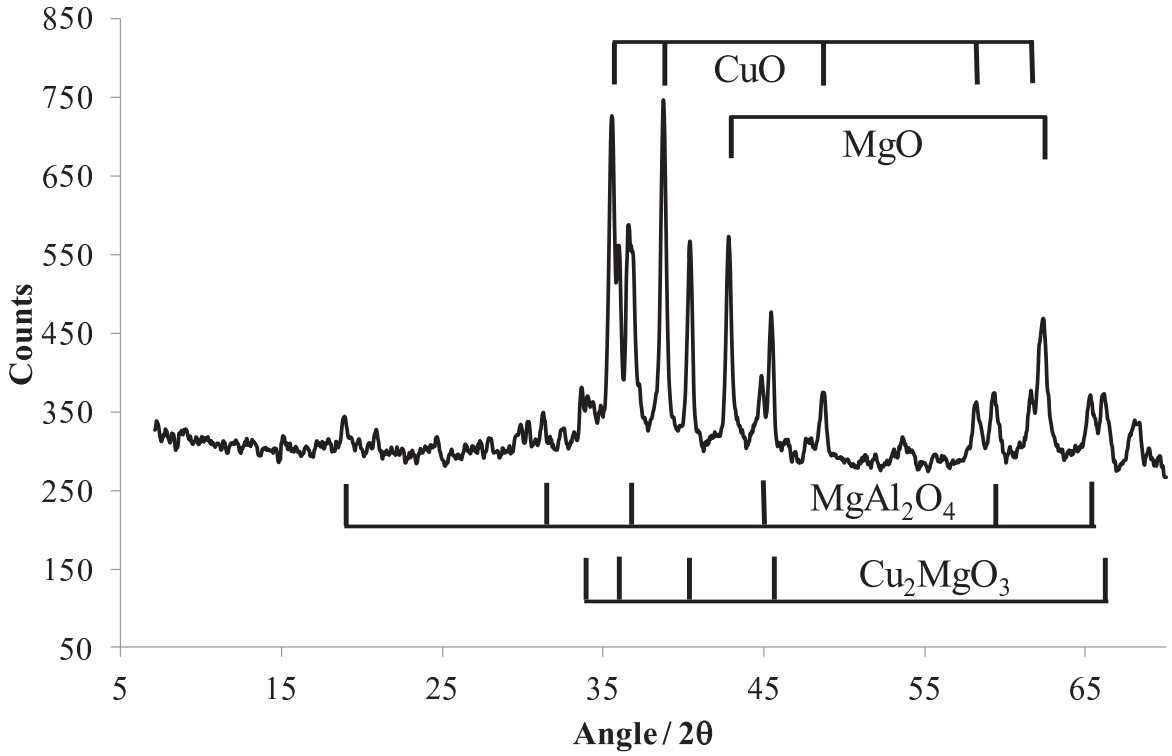
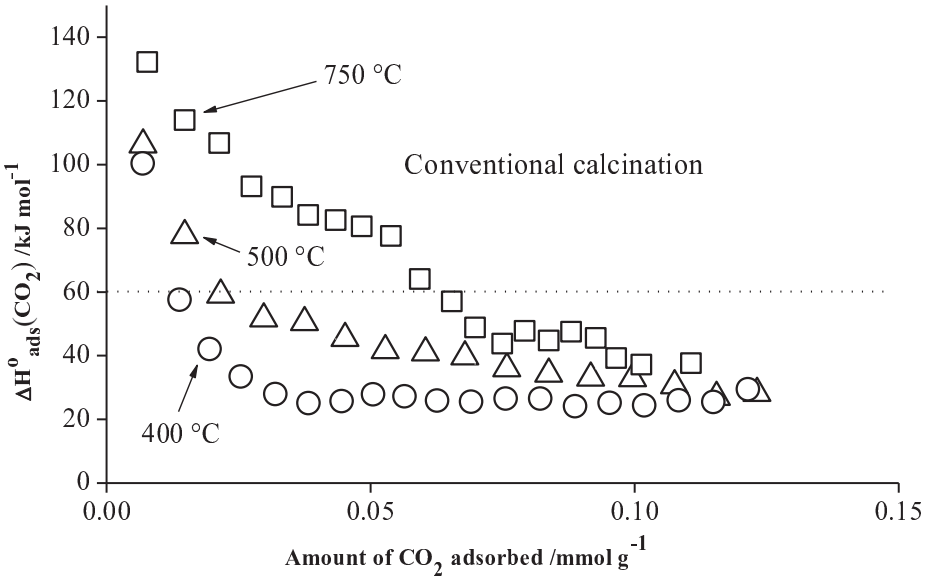


Fig. 4. Powder X-ray diffraction pattern for $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$ following calcinations under microwave heating at 750 ^{o}C.

Figure 5

FIGURE 5

a)



b)

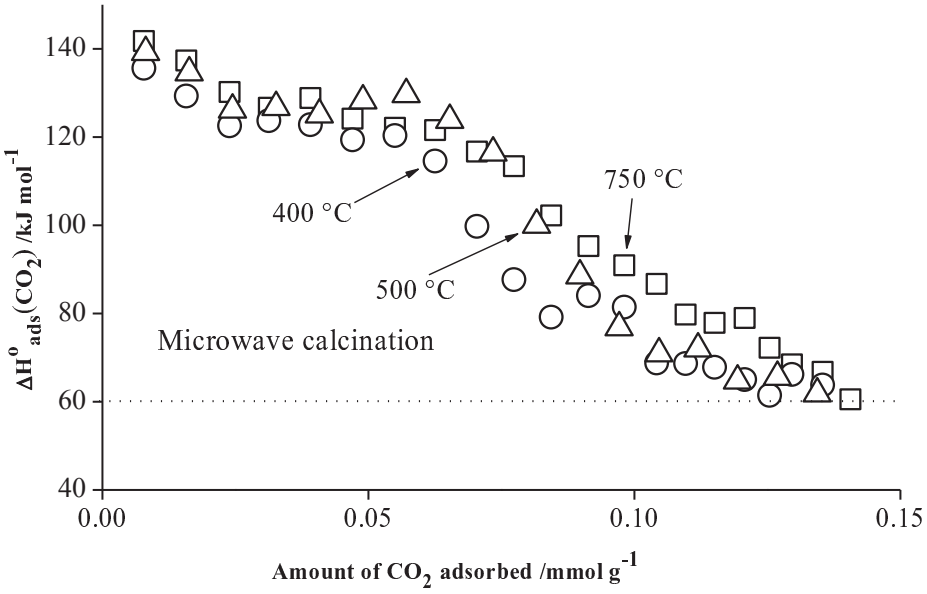


Fig. 5. Differential molar enthalpies of CO_2 adsorption vs. amount of CO_2 adsorbed at 120 ^oC for $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$ following calcination at 400, 500 and 750 ^oC under a) conventional and b) microwave heating.

Figure captions

Fig. 1. Temperature and power vs time plots for a copper(II)-containing hydrotalcite under microwave heating, a) where microwave power is increased linearly with time, showing sample temperature fluctuations and temperature runaway, and b) where the power is controlled to give a linear temperature increase.

Fig. 2. Powder XRD pattern of $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$.

Fig. 3. Powder X-ray diffraction patterns for $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$ following: a) conventional and b) microwave calcination, to the temperatures indicated.

Fig. 4. Powder X-ray diffraction pattern for $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$ following calcinations under microwave heating at 750 ^{o}C.

Fig. 5. Differential molar enthalpies of CO_2 adsorption vs. amount of CO_2 adsorbed at 120 ^{o}C for $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$ following calcination at 400, 500 and 750 ^{o}C under a) conventional and b) microwave heating.

Table caption

Table 1. Specific surface areas (BET) and catalytic activities of $Cu_{1.4}Mg_{4.4}Al_{2.2}(CO_3)_{1.1}(OH)_{16}$ following conventional (furnace) calcination and feedback-controlled microwave calcination.

Supplementary Material

Click here to download Supplementary Material: supplementary 30Mar2012.doc