



Microwave calcination of Cu/Mg/Al hydrotalcite catalyst precursor

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ABSTRACT

A copper-substituted hydrotalcite ($\text{Cu}_{1.4}\text{Mg}_{4.4}\text{Al}_{2.2}(\text{CO}_3)_{1.1}(\text{OH})_{16}$) 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.

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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].

Fig. 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 °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 °C to prevent the temperature runaway seen with no feedback-control.

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

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