Microwave-assisted Solid-state Reactions involving Metal Powders and Gases

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The high dielectric loss tangents of metal powders at 2450 MHz have been utilised to facilitate the syntheses of a range of metal chlorides, oxochlorides, bromides and nitrides by direct combination of metals with gases.

In recent years the acceleration of a wide range of chemical reactions using microwave dielectric heating techniques have been reported.[1–4] The great majority of these reactions have been in the solution phase where the high dielectric loss tangents of the polar solvents have been used to couple with the microwave energy. There have also been examples of solid-state reactions where the loss tangents of certain metal oxides have proved to be sufficiently large to couple with the microwaves and thereby provide sufficient thermal energy to raise the temperature of the reaction mixture to *ca.* 1000 °C and permit the reaction to proceed.[5–7] There have been very few reports, however, of microwave-assisted reactions involving metal powders. This may reflect a widespread belief that because metals within a microwave cavity may cause plasma discharges they are therefore an unsuitable component for microwave-assisted syntheses. The presence of solid metal samples and continuous metal films within a microwave cavity lead to large electric-field gradients and cause dramatic electric discharges. In contrast, however, metal powders can couple effectively with microwave fields at 2450 MHz[8] and heat up to temperatures in excess of 1000 °C in very short periods of time and without causing visible electric discharges.[9] The high loss tangents associated with metal powders results primarily from conduction mechanisms, although there may be additional contributions from localised plasma effects.[9] In a previous paper, we described how the high dielectric loss tangents of metal powders have been used to accelerate the syntheses of a wide range of metal chalcogenides.[10] Here we describe how the high dielectric loss tangents of metal powders have been used to facilitate the syntheses of a wide range of compounds by direct combination of metals and gases. The reactions of metal powders, which are volumetrically heated by microwave radiation, with gases has led to the convenient and rapid syntheses of a wide range of metal chlorides, oxochlorides, bromides and nitrides of transition metals. Although the results are of primary interest from a preparative point of view, they are relevant also to microwave-assisted catalytic reactions, where gases are passed over catalysts based on metal particles on inorganic supports.[11] Interesting differences in reaction time and selectivity have been reported for some of these reactions.

The remote nature of the coupling of microwaves with metal powders which have high loss tangents permits the development of alternative synthetic methodologies for these reactions, based on either a fluidised-bed technique, or by suspending the metal in a reaction vessel containing the reactive gas or gases. The types of apparatus developed for these syntheses are illustrated in Fig. 1. In the fluidised-bed apparatus (*a*), which is made wholly of silica, the metal powder is placed above the silica frit, and the reactive gas allowed to flow in a vertical direction. The flow rate of the gas is then adjusted to attain fluidised-bed conditions. In the suspended-sample apparatus (*b*) the metal sample is placed on the reaction platform, and the flask evacuated before filling with the reactive gas. A rather more conventional way of doing these reactions is to place the metal sample in a porcelain boat in a Schlenk tube, which is then filled with the reactive gas. In this case, if the product is

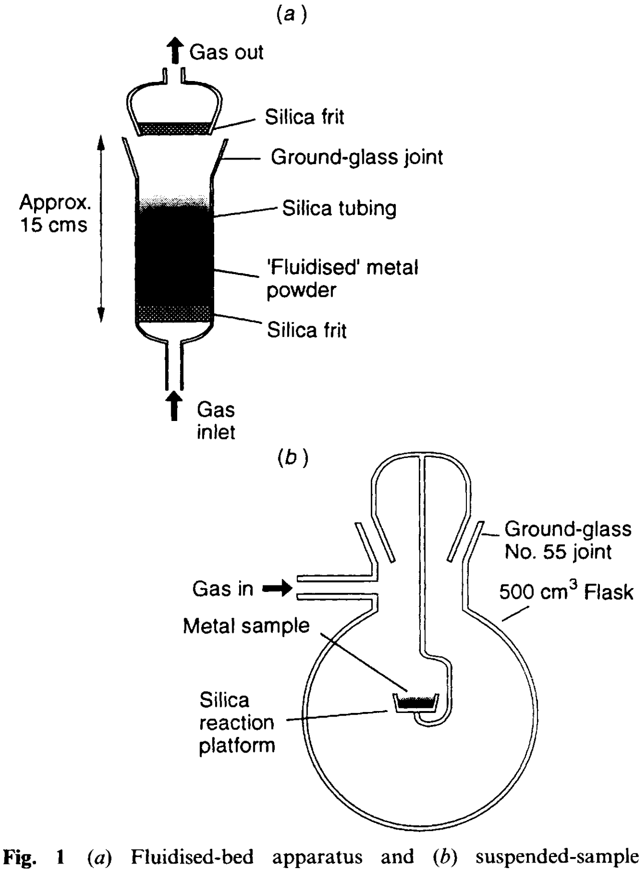

Fig. 1 (*a*) Fluidised-bed apparatus and (*b*) suspended-sample apparatus

Table 1 Details of the microwave-assisted reactions

Compound	Mass/g	Size/mesh	Gas	Method	Characterisation	Ref.
$CrCl_3$	2.08	−100	Cl_2	*a*	XRPD	12, 13
WCl_6	12.0	−16	Cl_2	*b* + *c*	IR, m.p. *c*, MS	14
$InCl_3$	3.21	−14	Cl_2	*a*	XRPD, *d*	15
$TeCl_4$	10.0	−100	Cl_2	*a*	XRPD, *d*	16
$WOCl_4$[e]	12.0	−16	$Cl_2 + O_2$	*b* + *c*	XRPD, *d*	17, 18
WO_2Cl_2[e]	12.0	−16	$Cl_2 + O_2$	*b* + *c*	XRPD, *d*	19, 20
TiN	50.0	−100	NH_3/N_2	*f*	XRPD	21
Cr_2N	20.0	−100	NH_3	*b,f*	XRPD	22
$TiBr_4$	5.0	−100	Br_2 + Ar	*b* + *c, f*	XRPD, IR, MS, *d*	23, 24
CuBr	8.0	Turnings	Br_2 + Ar	*b*	XRPD, *d*	25

[a] Suspended sample arrangement as described in the text. [b] A porcelain boat containing the metal is placed in a large Schlenk, containing the gas. Microwave power is applied, and further gas admitted as required, or, as in the case of Cr_2N, a flow system is created in a suitable silica vessel. [c] The air/moisture-sensitive product(s) is then purified by sublimation onto a cold finger in the same Schlenk. [d] Elemental analysis. [e] $WOCl_4$ and WO_2Cl_2 were formed in the same reaction, and separated by sublimation. [f] Fluidised-bed reactor as described in the text.

sublimable, it may be subsequently condensed onto a cold finger introduced into the top of the Schlenk tube. The three types of apparatus described were introduced into a multimode microwave cavity (Sharp R-5V11) operating at 2450 MHz (continuous power). In order to give greater control of the reactions, the microwave source for this cavity had been adapted to supply a continuously variable output between 0 and 700 W.

In the microwave cavity, the temperature of the metal powder may rise rapidly to over 1000 °C, and so allow the reaction to proceed. However, the total reaction time is not determined primarily by either this or the rate of heating of the metal powder, which may be as high at $100^\circ\ s^{-1}$,[10] but in most cases it is determined by the rate at which gas is able to reach the high temperature reaction sites.

The types of reaction studied are summarised in Table 1, together with the quantities of metal used, the metal mesh size, and the techniques used to characterise the products. The compounds in the Table had been synthesised previously using conventional techniques, and therefore were characterised using the literature powder X-ray diffraction (XRPD), infrared spectroscopy, melting point, mass spectral (MS) and elemental analytical data. Many of the compounds are widely used as starting materials for co-ordination and organometallic chemistry.

In solid-state reactions with metal powders the volumetric nature of the microwave dielectric heating sets a lower limit on the amount of metal powder required to drive the reaction. With the reactions described herein, the situation is slightly more complex. The amount of metal required in the fluidised-bed apparatus, for example, is determined more by the physical dimensions of the apparatus, and the rate of the gas flow required for fluidising the bed, than it is by the microwave characteristics of the sample. For example 5.0 g of titanium was required for the synthesis of $TiBr_4$, although smaller beds with suitable microwave applicators could lead to a significant reduction in this amount. When attempts are made to heat a sample of undispersed metal powder, the heating is not volumetric, but is a purely surface phenomenon which is limited by the skin depth of the metal used. At microwave frequencies the skin depth is typically of the order of microns[26] and if the metal powder is very fine (typically < 100 mesh) it is found that the heating is quite inefficient, since the surface exposed to the electromagnetic field is small relative to the total metal volume. When coarser metal powders are used ($\geqslant 100$ mesh), microwave heating is seen to occur on metal particles which are exposed and in limited contact with the bulk of the metal sample. Because of their limited contact, these particles do not disperse heat to the bulk by conduction quite so rapidly. Exothermic reactions may therefore be readily initiated with microwaves using coarse metal powders. Reactions which were not very exothermic could be driven to completion by progressively increasing the applied microwave power. In the case of the fluidised bed, the dispersion of the particles ensures that it is individual particles which are heated, since they do not lose heat by direct conduction to other, cooler particles. If excessive amounts of microwave power are applied to the fluidised bed, however, then it was found that arcing between the particles becomes a problem together with diffusion of the metal into the silica of the vessel walls. Fortunately, both of these problems are easily overcome by controlling the applied microwave power to a suitable level.

This preparative technique using microwaves offers many advantages over the corresponding conventional syntheses. The apparatus, once built, is extremely convenient to set up and use, and unlike many conventional methods, allows the worker to observe the reaction as it proceeds. The methodology therefore provides an attractive alternative to conventional tube furnace techniques. In addition, the products are formed in the vessel where they will be either used or stored. This is particularly useful if the products are particularly hazardous or air/moisture-sensitive, since the amount of handling and transferring is reduced to a minimum. For example, the apparatus shown in Fig. 1(*b*) can be used directly for the subsequent stage of the reaction involving the addition of a ligand, a Grignard reagent, *etc.* A further advantage which may be industrially significant involves the potential energy savings, since by this method, the power which is applied may be reduced to the minimum required to effect the reaction. It is envisaged that with more specialised applicators and reaction vessels, these energy savings could be further increased.

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