JOURNAL OF MATERIALS SCIENCE 31 (1996) 4479–4482

Low-temperature decomposition of hydrated transition metal chlorides on hydrous gel substrates

A. K. BHATTACHARYA, A. HARTRIDGE, K. K. MALLICK, C. R. WERRETT,
J. L. WOODHEAD
Centre for Catalytic Systems and Materials Engineering,
Department of Engineering, University of Warwick, Coventry, CV4 7AL, UK

The thermal decomposition of hydrated transition metal chlorides of nickel, cobalt and iron was studied on a highly dispersed alumina gel substrate. The salts were found to decompose at significantly lower temperatures than the unsupported materials. This was found to be as a result of strongly bound surface water, characteristic of this type of hydrous alumina. The resulting decomposed products were highly homogeneous and reactive, forming ceramic precursor compounds at much lower temperatures than conventional methods.

1. Introduction

The thermal decomposition of metal nitrate salts is a recognized procedure for the preparation of oxide ceramic precursor powders with superior fabrication properties. When hydrated thorium nitrate is heated at 490 °C, a crystalline water-dispersible powder is formed which can be used to prepare stable, colloidal dispersions containing up to 500 $g l^{-1}$ thorium oxide [1]. These sols can be gelled by dehydration and the gels calcined at 1200 °C to give oxide products with close to theoretical density.

In hydrated thorium nitrate, there are two types of water molecules; one is bound to the lattice and the other is simply co-ordinated water. During thermal processing, hydrolysis and polymerization of the salt occurs, leading to a lower temperature decomposition

$$MX_n + yH_2O \xrightarrow[\text{treatment}]{\text{Heat}} n[M(OH)_yX_{n-y}] + yHX \quad (1)$$

This mechanism of internal hydrolysis has also been found to be responsible for the lower temperature decomposition of alkali metal nitrates on silica gels [2]. This process of gel decomposition thus provides a useful technique for the preparation of mixed oxide compounds at low temperatures.

This paper shows that transition metal chloride salts, which are normally difficult to decompose, can be thermally decomposed at abnormally low temperatures when supported on hydrous gel substrates. This process is considered to occur by chemical mechanisms that are different from those previously reported for the heating of metal chloride salts. It is also shown that during the decomposition, the highly dispersed nature of the gel substrate also facilitates the formation of reactive ceramic precursors, leading to the formation of compounds at low temperatures.

2. Experimental procedure

2.1. Materials

AR-grade $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $FeCl_3 \cdot 9H_2O$ crystals were examined by thermogravimetric analysis and standard solutions of the salts were prepared, which were suitable for mixing with colloidal dispersions and ceramic powder forms of alumina. Alumina sols (~ 250 $g l^{-1}$ Al_2O_3) were prepared by dispersing Condea "Dispersal" powder in water or dilute (~10^{-2}M) hydrochloric acid.

2.2. The preparation of metal salts supported in gel substrates

2.2.1. Transition metal chloride on alumina

In a typical preparation, 50 ml $CoCl_2$ solution containing 2.1 g CoO equivalent was slowly added with stirring to 75 ml Condea alumina sol. Coagulation occurred but the colloidal state was maintained by dilution with water. The mixture in a total volume of 250 ml was stable to precipitation and was evaporated at 105 °C to give a bright blue water-dispersible gel.

Gels containing $NiCl_2$–Condea alumina and $FeCl_3$ on the same substrate were prepared using similar procedures.

The gels were examined by differential thermal and thermogravimetric analysis (DTA/TGA) and selected gels were heated in air to provide samples for X-ray diffraction studies.

2.2.2. α-Al_2O_3 reference samples

α-Al_2O_3 was finely ground and water added to form a paste. This paste was then dried to a constant weight at 105°C. $CoCl_2$ solution was then added to give the same proportion as above and the mixture again dried

0022-2461

at 105 °C. The gels were examined by DTA/TGA as above.

2.3. Characterization techniques

TGA analysis of the samples was carried out to determine the phase changes as well as the weight loss of gel samples using a Polymer Laboratories thermal analyser (Model STA1500). Flowing air was used as the normal atmosphere and the temperature was ramped at a rate of 10 °C min^{-1}.

X-ray powder diffraction (XRD) patterns for samples treated at various temperatures were recorded in the region of $2\theta = 5°–120°$ with a step scan of 0.1° min^{-1} on a Philips diffractometer (Model PW 1710) using CuK_α radiation. Cell parameters were calculated and further refined using linear regression procedures (Philips APD 1700 software) applied to the measured peak positions of all major reflections up to $2\theta = 90°$.

X-ray photoelectron spectroscopy (XPS) was used to determine surface chloride concentrations and dopant metal oxidation states. The analysis was performed using a Kratos XSAM 800 spectrometer fitted with a multichannel detector. Spectra were collected at a pressure of ~ 10^{-9} torr using MgK_α X-rays and in the fixed analyser transmission (FAT) mode. The powdered samples were contained in small dish-shaped sample holders and lightly pressed to present a flat surface to the exciting radiation. DS800 software was used for data processing and all binding energies have been referenced to the C1s peak at 284.5 eV to account for sample charging.

2.4. Chloride analysis

Samples of gel or oxide were boiled with 4M KOH and the leach liquor cooled and centrifuged. The supernatant liquor was acidified and the chloride content determined volumetrically by the Volhard method. Trace quantities were assessed by nephelometry.

3. Results and discussion

Differential thermal and thermo-gravimetric analysis of the unsupported hydrated chlorides is shown in Fig. 1. Cobalt chloride (Fig. 1a) shows a series of endothermic peaks between 50 and 166 °C corresponding to loss of water as seen in the percentage weight loss at these temperatures. Endothermic peaks at 712 and 727 °C correspond to the loss of chloride and the subsequent formation of Co_3O_4. Finally, a small oxygen loss and endotherm at ~ 930 °C, shows the transformation to CoO. Similarly, nickel chloride hydrate (Fig. 1b) shows loss of water at < 300 °C, chloride loss at 800 °C and its subsequent transformation to NiO. Iron chloride, however, shows a weight loss at 450 °C corresponding to loss of only one chloride, forming $FeCl_2$, which then sublimes at ~ 850 °C with no further decomposition [3]. Fig. 2 shows the thermal characteristics of the gel substrates used to support the transition metal chlorides. The Condea gel (Fig. 2a) shows a low-temperature weight loss and endotherm

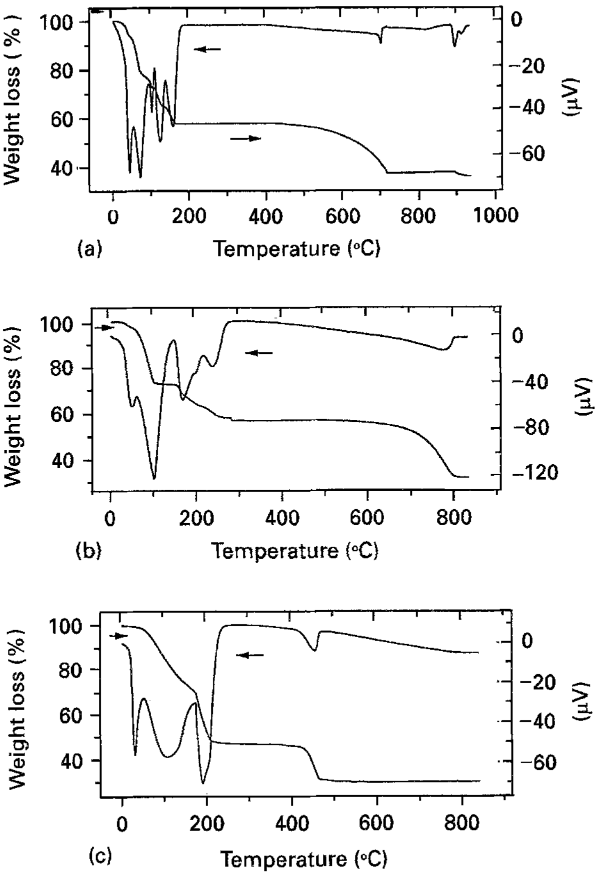

Figure 1 DTA/TGA of (a) $CoCl_2 \cdot 6H_2O$, (b) $NiCl_2 \cdot 6H_2O$, and (c) $FeCl_3 \cdot 9H_2O$.

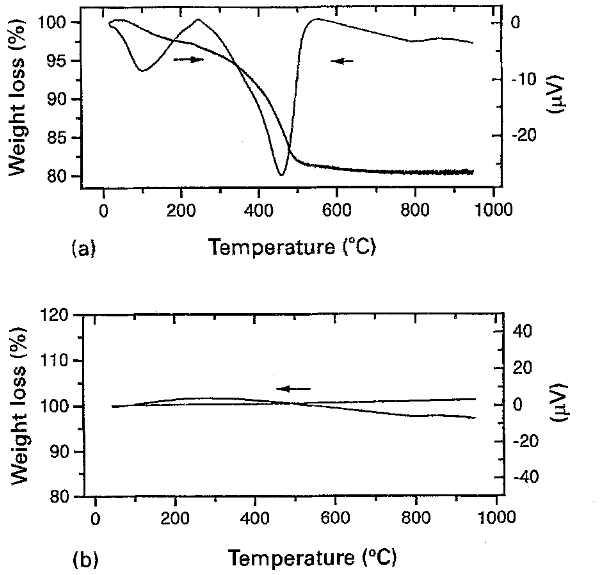

Figure 2 DTA/TGA of (a) Condea alumina hydrate and (b) alpha alumina.

corresponding to the acid sol-stabilizing species (nitric in this case), and holds onto water until 450 °C, where a huge endotherm can be seen. This also marks the transformation of the pseudo-bohemite AlOOH into γ-Al_2O_3. Alpha alumina, however, (Fig. 2b), which has been water soaked and dried at 105 °C, does not loose any weight or undergo any transformation up to 1000 °C.

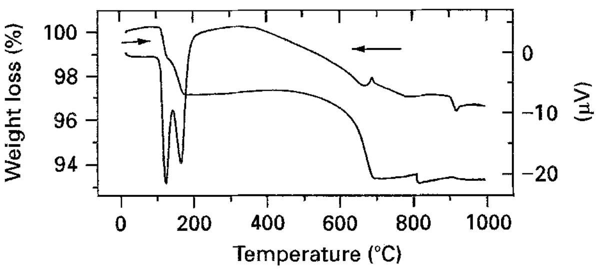

Figure 3 DTA/TGA of $CoCl_2 \cdot 6H_2O$ on alpha alumina.

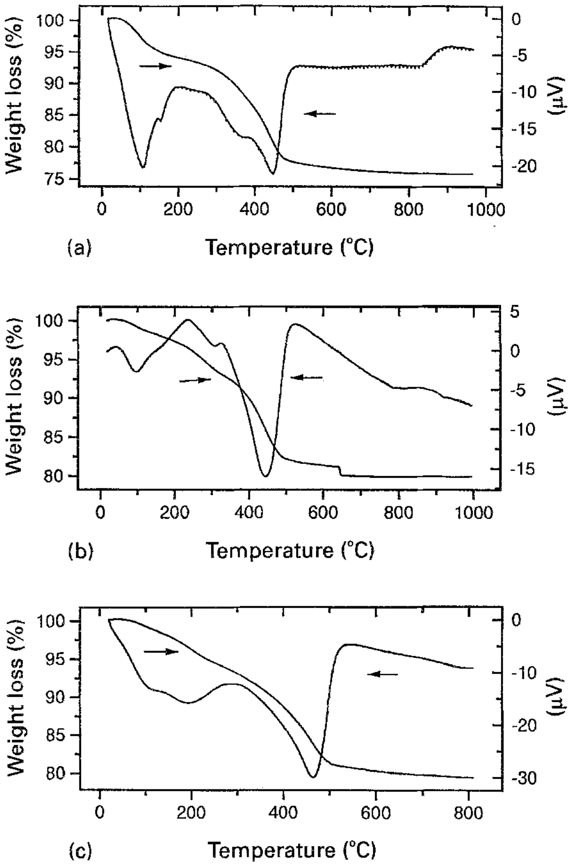

Figure 4 DTA/TGA of (a) $CoCl_2 \cdot 6H_2O$, (b) $NiCl_2 \cdot 6H_2O$, and (c) $FeCl_3 \cdot 9H_2O$; on condea alumina hydrate.

Fig. 3 shows the decomposition of cobalt chloride on the alpha alumina described above. Here the loss of water and chloride is similar to that of cobalt chloride alone, the alpha alumina having little effect on the chloride decomposition. The Condea/cobalt chloride system, however (Fig. 4a), shows an entirely different picture. In this system, the absence of any chloride loss at 700 °C indicates that the chloride is lost at 450 °C, coinciding with the loss of water from the pseudo-bohemite. This is confirmed by chloride analysis which shows a complete absence of chloride in gels calcined to 600 °C, moreover, XPS analysis shows a negligible amount of surface chloride. Also, the weight loss at 450 °C is 5–10% greater than that of the Condea gel alone and of the correct magnitude to explain chloride loss. Calcination of this material to 600 °C produced a bright blue powder which, because chloride is absent and Co_3O_4 is black, must indicate some interaction between the cobalt and γ-Al_2O_3. This is confirmed by X-ray diffraction versus temperature shown in Fig. 5. In the sample fired to 600 °C (Fig. 5a), the blue colour is due to the formation of a spinel type $CoAl_2O_4$ phase together with excess γ-Al_2O_3. At 900 °C, the blue colour is even more intense, resulting in a more prominent $CoAl_2O_4$ phase observed in the XRD pattern (Fig. 5b). Residual γ-Al_2O_3 is still found because only 10% CoO was added.

XPS of the calcined samples shows that there is only one component in the Co 2p spectrum with a Co 2p3/2 binding energy of 781.5 eV and a Co 2p3/2–Co 1/2 peak separation of 15.5 eV. The binding energy is higher than expected for CoO but close to that of $CoAl_2O_4$ and the peak separation is characteristic of cobalt in the + 2 oxidation state. This would indicate that hydration of the condea alumina, which is stable to 450 °C, is causing the breakdown of chloride at greatly reduced temperatures and the subsequent cobalt species is reacting readily with the small crystallites of gamma alumina.

Fig. 4b and c show the similar decompositions of nickel and ferric chloride, respectively, on Condea alumina. Again, chloride is decomposed at 450 °C, coinciding with the water loss of the gel. Moreover, there is no sublimation of the iron at high temperature as before, and chloride analysis shows the absence of any chloride at 600 °C. This suggests almost total chloride loss of the iron/alumina gel system at 450 °C. XPS analysis shows only trace amounts of chloride (< 0.1%) on the surface of the iron and nickel systems. Binding energy and peak separation data indicate that the nickel is in the + 2 oxidation state (Ni 2p3/2 = 856.3 eV, Ni 2p3/2-Ni2p1/2 = 18.3 eV) and present as $NiAl_2O_4$. However, for the iron system, peak fitting of the Fe 2p3/2 peak revealed two components at 710.6 and 712.8 eV in the ratio of ~ 4:1 in favour of the lower binding-energy component. The peak at 710.6 eV is characteristic iron in the + 3 oxidation state which is supported by peak separation data. Because Fe_2O_3 and the aluminate have similar binding energies it is not possible to distinguish between these moieties using XPS. It is suggested that the peak at 712.8 eV arises from the formation of an aluminate. XRD of the nickel and iron systems at 600 °C again shows the absence of any separate transition metal oxide phase, and the possible formation of an aluminate suggesting strong interaction with the alumina as in the cobalt system.

4. Conclusions

1. Gel decomposition reactions can be applied to transition metal halides that are volatile or difficult to decompose by conventional heat treatment.

2. The thermal decomposition of hydrated transition metal salts supported on hydrous gel substrates offers an interesting and novel approach to the preparation of crystalline metal oxides at lower-than-normal temperatures.

3. This low-temperature decomposition is associated with the presence of strongly bound surface

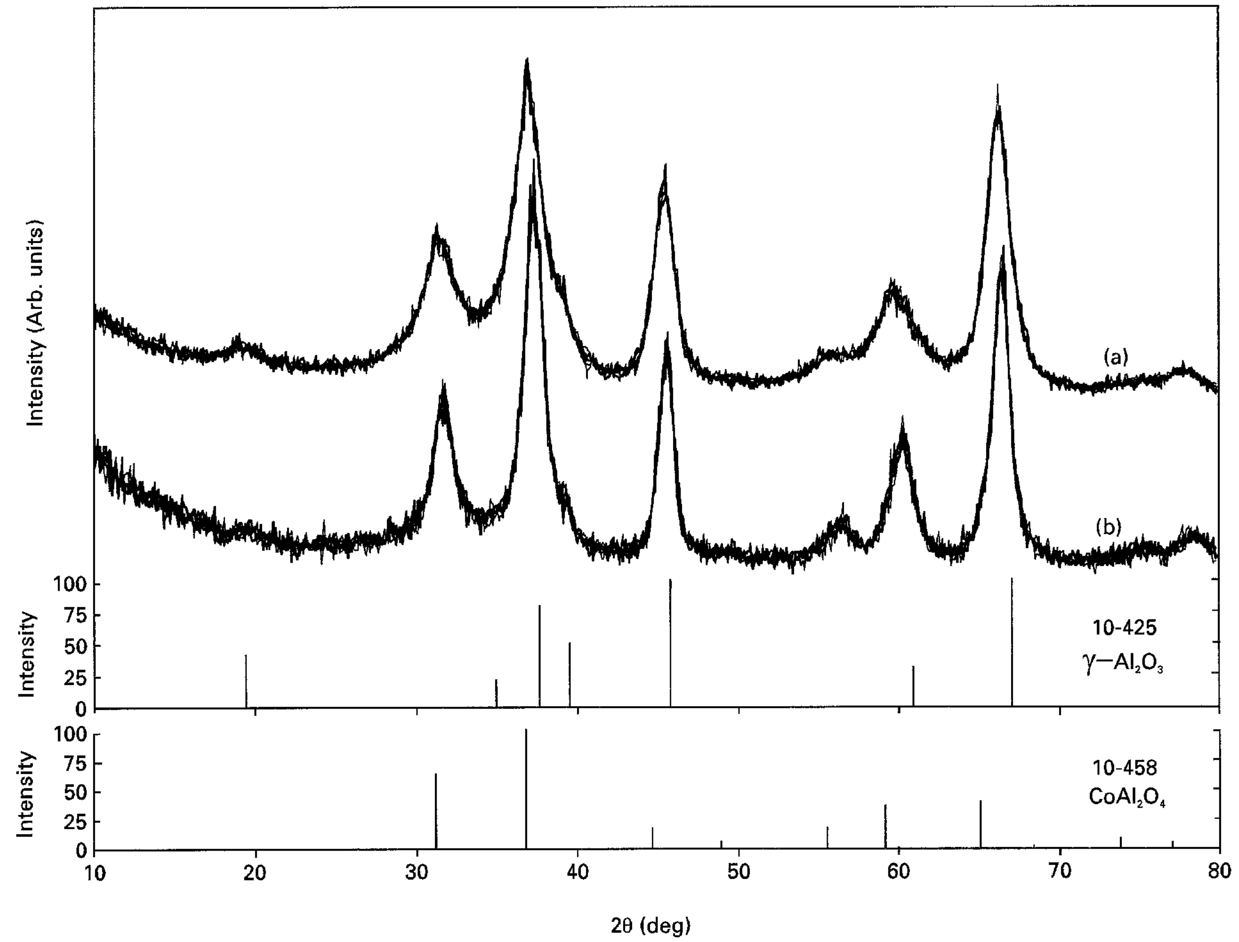

Figure 5 XRD patterns of $CoCl_2 \cdot 6H_2O$ decomposed on condea alumina heated to (a) 600 °C and (b) 900 °C.

water. The mechanism probably involves surface hydrolysis and polymerization.

References

1. D. E. FERGUSON, O. C. DEAN and D. A. DOUGLAS, "The Sol Gel Process for the Preparation and Remote Fabrication of Recycled Fuels", Third United Nations International Conference on the Peaceful Uses of Atomic Energy, Vol. 11 (1964) p. 237.
2. J. L. W. WOODHEAD, *J Phys. Col.* **C1–C12** Suppl. 2 (1986) 541.
3. "CRC Handbook of Chemistry and Physics", 64th Edn (1983–84), B-100.

Received 9 January
and accepted 18 March 1996