Thermal decomposition of co-precipitated oxide hydrates of zirconium and manganese

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Abstract

The thermal decomposition of mixed Zr–Mn oxide hydrates containing 0–0.3 mol of manganese was examined by means of simultaneous TG and DTA. When heated, these mixed hydroxides decompose to an amorphous oxide phase and subsequently crystallize to a cubic phase. These changes are accompanied by a broad endothermic peak at around 165–180°C and an exothermic peak between 450 and 700°C. The temperature at which the crystallization occurs depends on the manganese content. A linear increase was observed between manganese content and crystallization (exothermic peak) temperature. The enthalpy of crystallization, however, showed a decreasing trend (from 28.7 to 12.1 kJ mol^{-1}) with increasing manganese content within this range. Since no amorphous manganese oxide was formed when manganese oxide hydrate alone was heated, it is apparent that optimum concentrations of manganese (0.1–0.3 mol) in amorphous zirconia decrease the enthalpy of crystallization, thereby stabilizing zirconia in the cubic phase at low temperatures.

Keywords: Crystallization; Cubic phase; Decomposition; DTA; Oxide hydrate; Phase; Stability; TG; Zirconium oxide hydrate

1. Introduction

Zirconia is well known as a catalyst support for various metal oxides and metals. It is also known to accommodate distinct active metal ions in the lattice. Although it exists in different polymorphs such as monoclinic, tetragonal and cubic, several

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attempts have been made to stabilize zirconia as either a cubic or tetragonal structure [1–3] by incorporation of dopants such as Y^{3+}, La^{3+}, Mg^{2+}, Ca^{2+}, etc. More significantly, this kind of stable zirconia with a fluorite-type structure is useful as an oxygen sensor, a solid electrolyte and also as an oxidation catalyst [4–6]. Such versatility of stabilized zirconia is known to be due to the oxygen ion mobility caused by doping with lower valent metal ions or metal ions of different ionic sizes. A number of methods are known for the incorporation of various metal ions into the zirconia lattice [1,7]. Recently, we reported the low temperature stabilization of zirconia into the cubic phase by manganese through a co-precipitation route followed by calcination at 500°C [8]. Such a material appears to be a good catalyst in the complete oxidation of hydrocarbons and carbon monoxide.

In particular, in catalytic applications, co-precipitation as hydroxide is a favorable route for obtaining mixed oxides of zirconium and other elements, owing to its simplicity and the ease of formation of the requisite microstructure and texture after calcination. Accordingly, our preparation method follows a similar procedure to obtain stabilized zirconia with manganese in the lattice [8]. Since the preparation of this new material is mainly aimed at obtaining a good catalyst with a large surface area, it is important to optimize the temperature of calcination. An understanding of the mechanistic aspects of the thermal decomposition of these precursors is therefore relevant. The present study is aimed at such an understanding through a systematic TG and DTA investigation of the mixed hydroxides of zirconium and manganese. In addition, an attempt has been made to account for the role of manganese and the effects of various hydrolyzing agents on the thermal stability of zirconia.

2. Experimental

Mixed hydroxides of zirconium and manganese were prepared by co-precipitation, involving the rapid addition of ammonium hydroxide to stoichiometric amounts of mixed nitrate solutions of zirconium and manganese under constant stirring up to pH 8. The manganese content in the oxide was varied between 0 and 0.3 mol. After thorough mixing, ageing and filtration, the precipitates were washed several times and dried at 110°C for 24 h. The dried hydroxide precursors were stored in a desiccator to avoid adsorption of water. To study the effects of various hydrolyzing agents (precipitating agents), samples with 0.2 mol (20 mol%) of manganese in zirconia were prepared using tetramethylammonium hydroxide, tetraethylammonium hydroxide, sodium hydroxide and urea. Urea precipitation occurred at 100°C after 2 h. For comparison, a zirconium oxide hydrate sample without manganese dopant and a pure manganese hydroxide were prepared from the respective nitrates using ammonium hydroxide as precipitant.

Thermal analysis of the sample was carried out using simultaneous TG and DTA instrument (model 92, Setaram, France). About 40 mg of the powdered hydroxide precursor was placed in a platinum sample holder, 8 mm in diameter and 10 mm in height. The experiments were carried out at a uniform heating rate of 10°C min^{-1} up to 1000°C, and under 100 cm^3 min^{-1} flow of air or nitrogen.
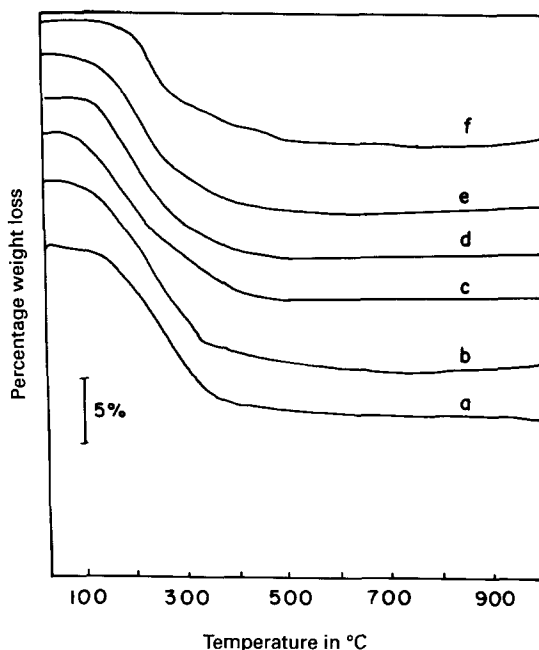
Fig. 1. TG profiles of the decomposition of (a) pure zirconium oxide hydrate, Mn–Zr co-precipitated oxide hydrate with (b) 0.05, (c) 0.1, (d) 0.2, and (e) 0.3 mol of Mn, and (f) pure manganese hydroxide, all precipitated with ammonium hydroxide at pH 8.

3. Results and discussion

3.1. TG and DTA of the oxide hydroxides

Figs. 1 and 2 show the TG and DTA plots, respectively, of the zirconium oxide hydrate (curve a), the Zr–Mn mixed oxide hydrates containing 0.05–0.3 mol manganese (curves b–e, respectively) and the pure manganese hydroxide (curve f), all obtained by precipitation using ammonium hydroxide. The major weight loss, in each case extending up to 300°C, is due to dehydration of the oxide hydrate. The observed weight loss given in Table 1 agrees very well with the theoretical values of the weight loss calculated from an assumption that the initial composition is $Zr_{1-x}Mn_xO(OH)_2$, where x is in the range 0–0.3. From an analysis of standard enthalpies of decomposition of different metal oxides and extrapolation to the standard enthalpy of formation of $Zr(OH)_4$, it has been recently suggested that only $ZrO(OH)_2$ or $ZrO_{1.5}(OH)$ can exist, and that $Zr(OH)_4$ is not stable at room temperature [9]. In the case of Mn–Zr mixed oxide hydrates, the agreement between the calculated and observed values confirms the initial composition to be that of an oxide hydroxide.
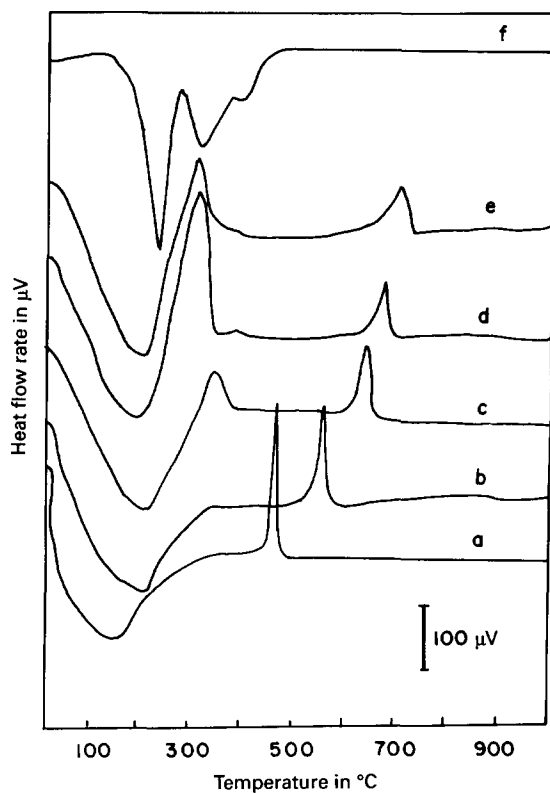
Fig. 2. DTA profiles of the decomposition of zirconium oxide hydrate, Mn–Zr oxide hydrate and manganese hydroxide. Details of the samples are given in Fig. 1.

Table 1
Weight loss, peak maxima and enthalpy of crystallization of zirconium oxide hydrates with different manganese prepared by co-precipitation with ammonium hydroxide

Precursor hydrate sample	Weight loss (observed) in wt%	Weight loss (calculated) [a] in wt%	Peak maxima in °C		Enthalpy in kJ mol^{-1}	
			Endo	Exo	Endo	Exo
Zr oxide hydrate	12.55	12.69	165	467	−121	28.2
Zr–Mn (0.05) [b]	12.70	12.90	178	545	−142	22.6
Zr–Mn (0.1)	13.05	13.08	180	603	−120	16.7
Zr–Mn (0.2)	13.40	13.44	173	667	−129	12.1
Zr–Mn (0.3)	13.80	13.81	143	687	−65	12.1

[a] Assuming the initial composition to be $Zr_{1-x}Mn_xO(OH)_2$. [b] Concentration of Mn (mol) in parentheses.

Table 2
TG and DTA data on the co-precipitated Mn–Zr oxide hydrates (0.2 mol manganese) prepared using different hydrolyzing agents

Hydrolyzing agent	Weight loss in wt%	Peak maxima in °C		Enthalpy in kJ mol^{-1}	
		Endo	Exo	Endo	Exo
Ammonia	13.40	173	667	-129	12.1
Tetramethylammonium hydroxide	19.44	107	691	-48	3.8
Tetraethylammonium hydroxide	32.49	113	633	-31	7.8
Sodium hydroxide	10.84	178	674	-85	11.8
Urea	23.40	193	568	-156	24.0

For both zirconium oxide hydroxide and the Mn–Zr mixed oxide hydroxide, dehydration is accompanied by a large endothermic peak in the range 100–300°C. The peak maxima are recorded between 150 and 180°C for all the samples and the calculated heats are in the range 120–142 kJ mol^{-1} (Table 1). The samples with higher manganese loadings, i.e. 0.2 and 0.3 mol of manganese in ZrO_2, show two endothermic peaks which are not well resolved (Fig. 2). This is probably due to separate or individual dehydration of the Mn–Zr oxide hydroxides from the mixed phase.

Apart from ammonium hydroxide, other precipitating agents such as sodium hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide and urea were also used to obtain the mixed hydroxides. Table 2 presents the details of our TG and DTA observations on the decomposition of mixed Mn–Zr oxide hydrates (with 0.2 mol manganese) so obtained. Weight loss increases with an increase in the molecular weight of the alkyl group of tetraalkylammonium hydroxide. The alkyl groups are probably absorbed or trapped inside the micellar network of the oxide hydrates. It is hence difficult to assign the exact initial composition of the mixed oxide hydrates. The weight loss observed for the mixed Mn–Zr oxide hydrate varied from 32% in the case of tetraethylammonium hydroxide to about 10% in the case of sodium hydroxide. This indicates that the initial composition may vary from $Zr_{0.8}Mn_{0.2}O(OH)_2$ to $Zr_{0.8}Mn_{0.2}O_{1.5}(OH)$. In fact, stoichiometric compounds of zirconium oxide hydrates are rather difficult to prepare and are very unstable substances, whose composition depends strongly on the conditions of preparation [10].

Fig. 3 gives a comparison of the TG and DTA profiles of a Mn–Zr oxide hydrate freshly precipitated by tetramethylammonium hydroxide, and the same sample after repeated washings with deionized water. The weight loss due to the decomposition is considerably lower in this sample. In addition, a large exothermic peak observed around 150–280°C (well before crystallization) is attributed to the presence of methyl or methylammonium species trapped inside the mixed oxide hydrates.
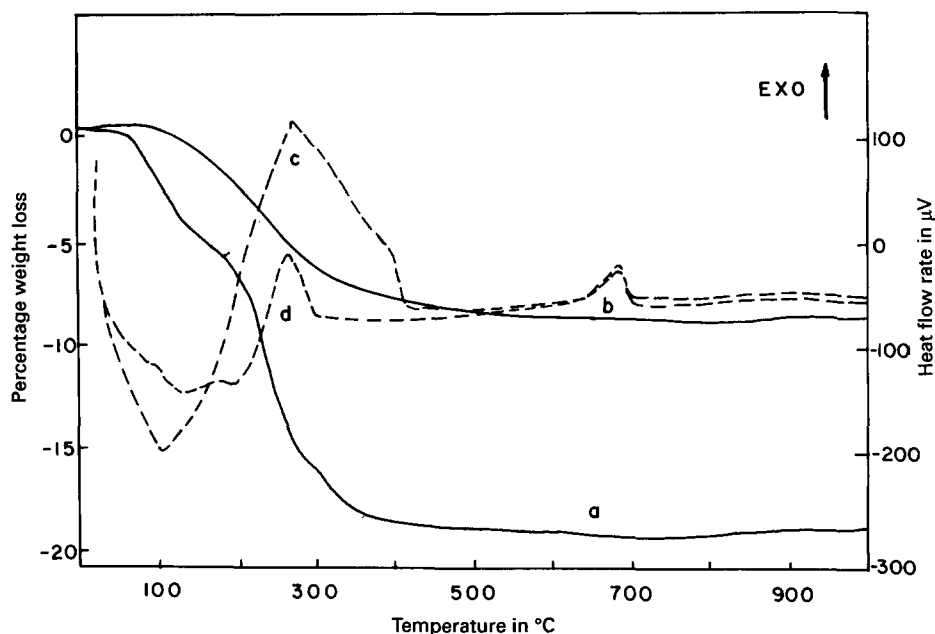
Fig. 3. TG and DTA curves of 0.2 mol Mn–Zr oxide hydrates prepared using tetramethylammonium hydroxide as precipitant. (a,b) TG curves and (c,d) DTA curves refer to precipitates after normal washing and repeated (> 10 times) washing, respectively.

3.2. Crystallization and the glow exotherms

After the dehydration is almost complete, the transition from amorphous to the crystalline phase is accompanied by an exothermic peak in the temperature range 450–600°C for all the samples apart from manganese hydroxide (Fig. 2). Similar observations have been reported in the preparation of Y^{3+}-stabilized zirconia [9]. The exothermic peak temperatures for all the samples are given in Table 1. The water content at the initial temperature of the exotherm was very small in all cases. The shift between the initial and peak temperatures of all the exotherms increases with manganese content. The difference between the initial and the final temperatures also increases, showing broadening of the exothermic peaks. The enthalpy of crystallization calculated from the integrated intensity of the DTA exotherms was found to be 28 kJ mol^{-1} for pure zirconia, agreeing well with the value reported by Livage et al. [11]. On going from pure zirconium oxide to mixed Mn–Zr oxide samples containing different concentrations of manganese, there is a tendency for the exotherms to shift to higher temperatures. Considering the peak maxima, there is almost a linear increase in the exothermic peak temperature with increasing manganese content in the zirconia, as seen in Fig. 4. A similar observation with yttria-stabilized zirconia has been reported recently by Tagawa et al. [9]. At first sight, this seems to indicate that the crystallization is hindered by the presence of manganese in the amorphous zirconia. However, the enthalpy of crystallization
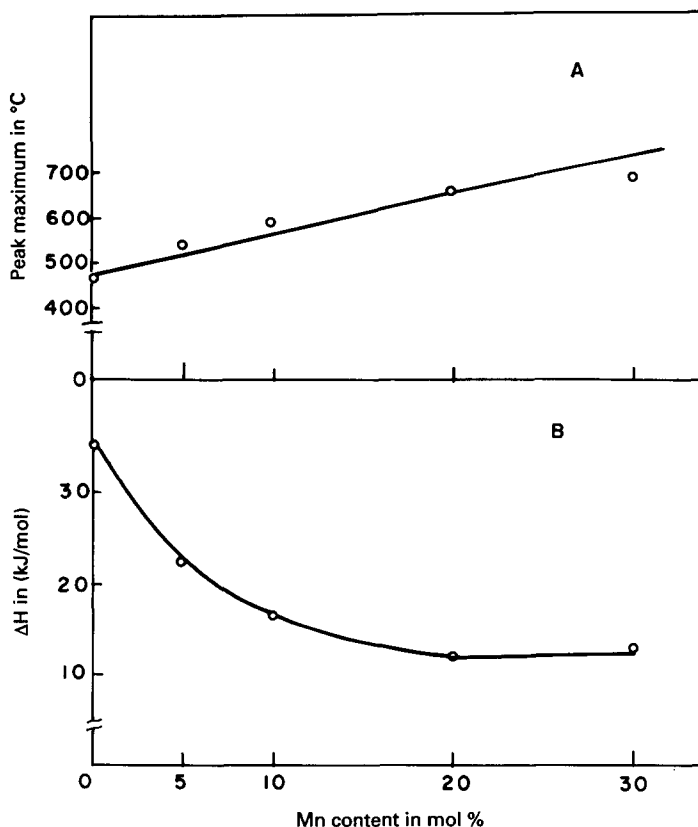
Fig. 4. Influence of manganese content in zirconium oxide hydrate on (A) the exothermic (crystallization) peak maxima, and (B) the enthalpy of crystallization.

decreases progressively from 28 kJ mol^{-1} of ZrO_2 for the pure ZrO_2 sample to 12.1 kJ mol^{-1} of ZrO_2 for samples with 0.2 mol of manganese in zirconia and stabilized at the same value for 0.3 mol of manganese-containing sample (Table 1). This transformation from the amorphous to the crystalline phase occurs just after completion of the dehydration step in all the samples, since no weight loss is observed in this region. This exotherm could be a characteristic feature of either the crystallization alone or the glow phenomenon [12], or both of these occurring simultaneously. When the manganese oxide hydrate alone is decomposed, no exothermic peak is observed and no amorphous phase is formed. It is, therefore, possible that when MnO_2 is dissolved in amorphous zirconia, the enthalpy of crystallization of the amorphous to the crystalline cubic phase decreases.

In the case of pure zirconium oxide hydrates, the observed exotherm at around 471°C is very sharp. A similar observation was reported earlier [12] and has been attributed to the simultaneous occurrence of a glow phenomenon and crystallization. Such an exotherm was also observed for other metal oxides, including ferric oxide and chromium oxide [13]. The glow phenomenon is believed to be a visible

manifestation of the coalescence of primary colloidal particles to larger masses with consequent release of surface energy [14]. In the case of pure zirconium oxide hydrates, such a crystallization often leads to a monoclinic ZrO_2 phase (X-ray diffraction). A decrease in the enthalpy of crystallization with increase in manganese content indicates that the glow phenomenon slowly decreases with increasing manganese content. Thus, manganese contributes significantly towards the decrease in exothermicity of the glow and crystallization results in the formation of cubic ZrO_2 [8]. Similar quelling of the glow was attributed to adsorption of one oxide onto the surface of the other when two oxides were mixed together [14]. In the present case, it is the formation of solid solutions of zirconium and manganese mixed oxides which is probably responsible for the decrease in glow.

3.3. Texture and phase transformation

The controlled calcination of the precursors leads to transformation from an amorphous to a crystalline phase. This process may be treated as proceeding in two steps: the first is the formation of the initial microcrystalline phase and the second the sintering of the small crystallites into bigger crystals. A large enthalpy of crystallization will facilitate the second step. Since the glow phenomenon results in crystal growth, a loss of surface area and profound alteration in the electronic properties of the crystalline materials can be expected. Hence, it is essential to control this phenomenon [13]. The manganese incorporated in zirconia appears to control this phenomenon and, as a result, there is a substantial increase in the surface area of the samples formed. On increasing the manganese content, the surface area increases (from 70 to 110 $m^2 g^{-1}$) for the samples calcined at 500°C [8]. In the X-ray diffraction profiles of the samples, significant peak broadening is observed with an increase in manganese content, indicating a decrease in the crystallite size [15]. Hence, this exothermic peak observed in DTA can be ascribed to the phase transformation from the amorphous to the crystalline phase only, and not to the glow phenomenon. Apart from the formation of the small crystallites, presence of mesopores was also observed in the manganese-stabilized zirconia samples. These are stable in the cubic phase up to 750°C and are found to be active in the total oxidation of hydrocarbons (C_1–C_4) and carbon monoxide [15].

4. Conclusions

In the manganese containing zirconium oxide hydrates (0–0.3 mol manganese) prepared by the co-precipitation method using ammonium hydroxide, the initial composition corresponds to $Zr_{1-x}Mn_xO(OH)_2$, as seen from the TG results of the decomposition of these hydroxides. There is a tendency for manganese to hinder the crystallization of zirconia to a cubic phase, as the DTA peak maxima of the exotherms shift progressively to higher temperatures when the manganese content increases in the samples. Nevertheless, the enthalpy associated with the crystallization process decreases with manganese content. On heating, a solid solution of

manganese in amorphous zirconia leads to the formation of $Zr_{1-x}Mn_xO_2$, stabilized in the cubic phase with a fluorite-type structure, having a larger surface area and smaller crystallite size.

Acknowledgment

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