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APPLICATION OF THERMAL ANALYSIS IN SURFACE CHEMICAL INVESTIGATION OF ZIRCONIA GELS

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ABSTRACT

Thermoanalytical techniques can be most valuable in relating the chemical history and the role of precipitants to the surface chemical properties of gels and have been used to elucidate the origin of porosity in zirconia gels. The aspects discussed are: (a) aqueous chemistry and polymerization, (b) role of precipitating conditions on development of surface properties, (c) application of thermoanalytical techniques to elucidate the origin of porosity and (d) study the glow phenomenon in zirconia gels.

The surface and microstructural properties of zirconia gels precipitated from zirconyl chloride solution by NH_3 gas, $NaHCO_3$ and NH_4HCO_3 were characterized by nitrogen and water adsorption, X-ray diffraction and electron microscopy. NH_3 yielded a microporous gel that was thermally unstable whereas sodium bicarbonate gave a mesoporous solid that increased in mesoporosity with increasing temperature (20 - 450^{o}C). The gel resulting from ammonium bicarbonate showed an intermediate behaviour.

TG, DTA and EGA have confirmed that the development of a mesopore system in the $NaHCO_3$ precipitated gels can be directly related to the retention of a small amount of CO_2 as a bidentate ligand in the structure of the gel; this would explain the stability and development of mesoporosity. Thermoanalytical techniques have also been useful in showing that for ammonia-precipitated gels the micropore volume is essentially protected by monodentate H_2O and NH_3 ligands.

The chemical history of different zirconia gels can also be related to their crystallization during glowing by thermoanalytical techniques. For carbonate-precipitated gels the endothermic effect of CO_2 evolution compensates the exothermic glow phenomenon but crystallization progresses despite the absence of the exotherm. The lower limit of the exotherm was established as 375^{o}C. It is also shown that ligands derived from various precipitants incorporated in the gels strongly influence their high-temperature behaviour. The observed properties are interpreted on the basis of a defect structure involving O^{2-} vacancies generated through the removal of these ligands. These studies suggest that a similar approach would be very valuable in investigating other hydrous oxide gel systems.

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Most surface chemical investigations involving oxides have been carried out on the so-called "active oxides", (e.g. silica, alumina, titania, magnesia, uranium oxides, chromia and thoria), because of their catalytic properties and their considerable industrial importance. Extensive studies published include the various preparative methods employed and their relation to the subsequent surface properties of the oxides. A logical extension of these studies would be to the Group IV elements of the Periodic Table. Of these silica and titania have been extensively studied, but the next oxide in the series, zirconia (ZrO_2), has received comparatively little attention. For this reason the emphasis of this review will be on the factors that influence the surface chemistry of ZrO_2 and on the thermoanalytical techniques that can help in elucidating the origin of porosity in zirconia gels.

Surface chemical techniques (viz., adsorption studies using different adsorbates) help to characterize surface area, porosity, specificity of interaction between the surface and the adsorbates while X-ray crystallographic and electron microscopic studies reveal structural and microstructural features. These techniques, however, disclose little about the origin of porosity in zirconia gels. On the other hand, thermoanalytical techniques such as thermogravimetry (TG), differential thermal analysis (DTA) and evolved gas analysis (EGA), offer a unique opportunity of relating the chemical history and the role of precipitants to the surface chemical properties, thus revealing the origin of porosity in zirconia gels. A further application of DTA is in the study of glow phenomenon and the defect structure in zirconia gels. Hence, the following aspects of thermochemistry and surface chemistry of zirconia gels are considered below: (a) aqueous chemistry and polymerization, (b) role of precipitating conditions in development of surface properties, (c) application of thermoanalytical techniques to elucidate the origin of porosity and (d) the study of glow phenomenon in zirconia gels.

Unlike Cr, Cu, Ti and Sn, which exhibit variable valencies, zirconium occurs almost exclusively in its compounds with the oxidation number 4+. Hence, its chemistry in general and surface chemistry in particular is likely to provide a model system, uncomplicated by variable oxidation states. The precipitation of the oxides is an important step in their preparation, since the surface area, pore size, development of porosity and resistance to sintering are all strongly influenced by the conditions employed. Thus, the presence of a unique oxidation state is helpful in providing a clearer view of the effects of the precipitation conditions and precipitating agents on the subsequent surface properties.

Hydrous zirconia can be prepared with different zirconium compounds but the most frequently chosen source of zirconia is the zirconyl solution, particularly zirconyl chloride in which the zirconium ion is coordinated by four OH and H_2O groups, the lone pair of electrons being provided by the oxygen (ref, 1, 2). The smallest unit present is the tetrameric complex (Fig. 1). Moreover, the Zr-Cl bonding that occurs in zirconyl chloride solution is absent (ref. 3).

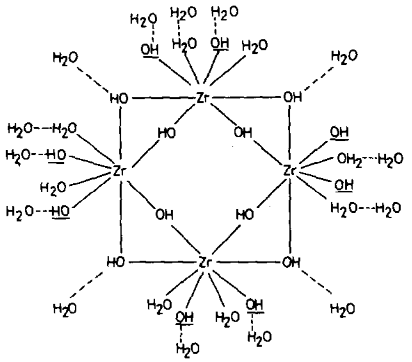


Fig. 1. Freshly formed single tetramer of pure hydrous zirconium oxide, zero charge.

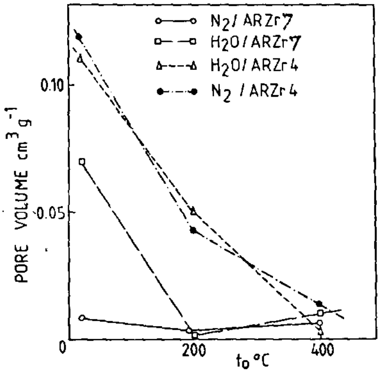
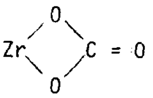


Fig. 2. Variation of pore volumes of ammonia and ammonium bicarbonate precipitated gels, ARZr4 (N_2 and H_2O) and ARZr7 (N_2 and H_2O), respectively.

The behaviour of zirconium complexes in solution is governed by hydration, hydrolysis and polymerization (ref. 2 - 6) that leads eventually to a three-dimensional network resulting in a gelatanous precipitate of "hydrous" zirconia $ZrO_2 . xH_2O$ (ref.7 - 10). When zirconia is precipitated with NH_4OH or NH_3 gas, the NH_4^+ or NH_3 ligand present in solution can replace certain aquo groups from the hydration sphere and compounds of the type $ZrO_2.xH_2O. yNH_3$ are likely to be generated (ref. 11). When precipitated with solutions of NH_4HCO_3 or $NaHCO_3$ carbonatozirconates are the likely products (ref. 12). There is little published information on zirconium carbonates, although as early as 1825 Berzelius (ref. 13) prepared $ZrOCO_3 . 2ZrO_2 . 8H_2O$ and recent studies (ref. 12, 14, 15) suggest that complex carbonato-zirconium anions form bidentate oxygen linkages of the type



As conditions of precipitation affect the polymerization of the zirconia gels they would also have a significant effect on its surface properties, particularly surface areas and pore structure (ref. 16 - 21). However, two problems arise in attempting to relate precipitating conditions to subsequent surface properties of zirconia gels from the published literature. Firstly, there is very little information on the exact conditions and detailed chemical history of the gels and, secondly, even if reported, there is a lack of rigorous control of the conditions of preparation of the gels. For this study, therefore, gels were prepared under strictly controlled conditions using zirconyl chloride and various precipitating agents. The agents employed at pH 7.0 were sodium bicarbonate solution, ammonia gas and ammonium bicarbonate solution, but, to study the influence of pH, samples were also prepared using ammonia gas at different pH values. Details of the preparative procedures have been discussed elsewhere (ref. 11, 22 - 25) but to aid identification for the present purpose, the samples studied, their designation, method of preparation and behaviour on thermal treatment are tabulated in Table 1.

TABLE 1

Preparation and thermal data for the zirconia gels studied

Sample	Precipitant	pH of preparation	Heating atmosphere	% Weight loss at			
				250°C	500°C	750°C	900°C
ARZr2	$NaHCO_3$	7.0	-	-	-	-	-
ARZr3	$NH_3(g)$	5.0	Air	29.4	31.0	31.3	31.4
			N_2	29.4	31.3	31.8	31.8
			H_2	30.3	31.9	32.6	-
ARZr4	$NH_3(g)$	7.0	Air	27.8	29.3	29.9	30.0
			N_2	28.8	30.3	30.8	30.8
			H_2	26.2	32.6	36.3	-
ARZr5	$NH_3(g)$	9.0	Air	29.2	29.4	30.6	30.8
			N_2	28.6	30.1	30.3	30.4
			H_2	29.1	30.4	30.8	-
ARZr6	$NH_3(g)$	11.0	Air	30.2	31.6	32.0	32.0
			N_2	30.2	31.8	32.1	32.2
			H_2	31.0	32.5	32.8	-
ARZr7	NH_4HCO_3	7.0	Air	26.2	29.5	31.0	31.2
			N_2	26.7	31.0	31.0	32.2
			H_2	26.2	29.5	32.6	33.4

Gels precipitated by NH_3 gas were exclusively microporous (ref. 22, 24, 25) as shown by water and nitrogen isotherms, representing Type 1 in the BDDT (ref. 26) classification. Isotherms also clearly demonstrated an increase in the micropore volume and micropore size with increasing pH (ref. 25). For the pH7 gel outgassed at 25 and 200°C, there is a good agreement between the pore volumes available to both nitrogen and water molecules (Fig. 2). The microporosity is, however, complex as the gels exhibit low pressure hysteresis (ref. 11, 24) and undergo ageing. Typical water isotherms are shown in Fig. 3.

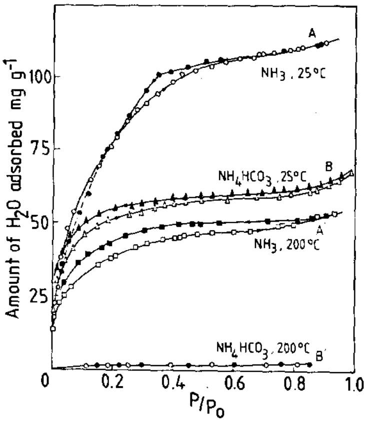


Fig. 3. Water adsorption-desorption isotherms on hydrous zirconia gels at different outgassing temperatures. Precipitants used were ammonia and ammonium bicarbonate.

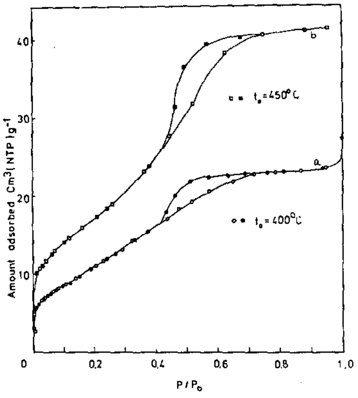


Fig. 4. Nitrogen adsorption-desorption isotherms on sodium bicarbonate precipitated gels, at two outgassing temperatures, indicating mesoporosity.

The drastic loss of micropore volume in ammonia-precipitated gels at 400°C (Fig. 2) is similar to that observed with chromia under the same condition (ref. 27), and may be associated with the reorganization of the structure prior to crystallization and the onset of the glow phenomenon, which occurs at _ca_ 470°C for zirconia (ref. 23).

When NH_4HCO_3 is the precipitant the gels are mostly microporous when outgassed at 25°C but when outgassed at 200°C, the micropore structure collapses dramatically (Fig. 3). Moreover, in contrast to ammonia-precipitated gels, the ammonium bicarbonate precipitated gels show an increase in their pore volumes in the range 200 - 400°C, (Fig. 2). The significance of this will be discussed later.

The surface properties of the gels prepared by $NaHCO_3$ as precipitant are distinctly different, as shown by the representative isotherms in Fig. 4. These conventional Type IV isotherms in the BDDT classification (ref. 26) represent well defined E-type hysteresis loops as classified by de Boer (ref. 28) and hence represent mesoporosity. The water isotherms show similar mesoporosity (ref. 11), and the BET surface areas obtained by water and nitrogen are compared in Fig. 5. Surface areas or pore volumes of these gels when outgassed at 400°C show characteristic behaviour. For ammonia precipitated gels, the microporosity collapses whereas the ammonium bicarbonate product shows a small increase in pore volume and the $NaHCO_3$ precipitate is mesoporous with very high surface areas at comparable temperatures.

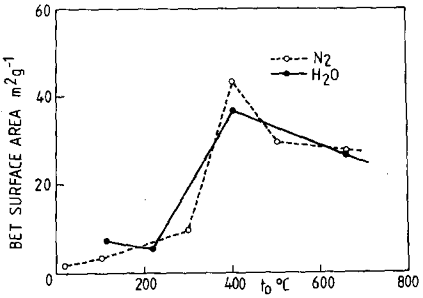


Fig. 5. Variation of BET surface areas obtained with water and nitrogen on sodium bicarbonate precipitated hydrous zirconia gel with outgassing temperatures.

Thermoanalytical (TG, DTA and EGA) study of the zirconia gels have proved most helpful in explaining the above behaviour. As the results have been discussed in detail elsewhere (ref. 11, 23) only the salient features are summarised below. Initial experiments established that, for the samples studied, the weight loss observed with increasing temperature was sensitive both to the rate of heating and to the nature of the carrier gas. Typical TG curves for samples prepared with the three precipitants employed, measured with a nitrogen flow, are illustrated in Fig. 6 (a), while the DTG curves for the same samples under the same conditions are depicted in Fig. 6 (b). All TG curves indicate a final weight loss of about 30% of the initial sample weight, although differences occur between individual samples regarding the

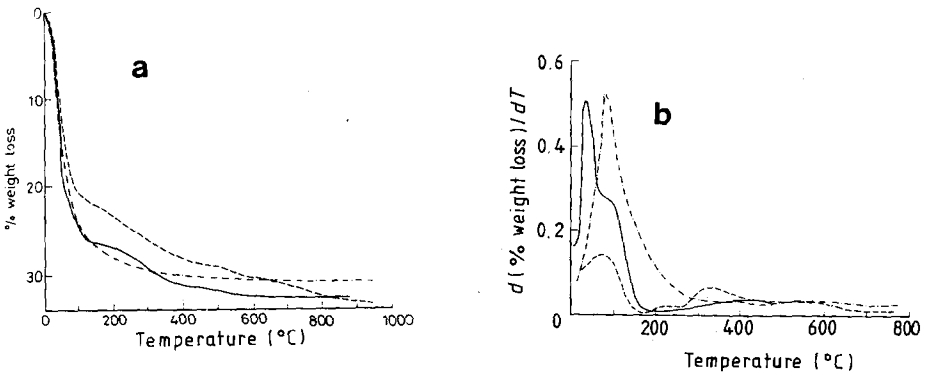


Fig. 6. (a) Typical TG curves for zirconia gels prepared with various precipitants. All samples prepared at pH7; curves measured with nitrogen gas flow of 10 cm^{3}min^{-1} at a heating rate of 10^{o}C min^{-1}. (b) The corresponding DTG curves for the same samples.---, ARZr2 ($NaHCO_3$); -.-. ARZr4 (NH_3); ——ARZr7 (NH_4HCO_3).

various temperature ranges over which significant weight loss occurs. Thus, the ammonia-precipitated sample (ARZr4) exhibits the greatest weight loss over temperatures up to 250^{O}C, a final constant weight being attained at about 350^{O}C. All samples prepared with this precipitant behaved similarly irrespective of the pH of preparation. In contrast, although the zirconia gel sample precipitated with sodium bicarbonate (ARZr2) loses some 20% of its initial weight below 100^{O}C, thereafter further weight loss occurs gradually, 30% weight loss being attained only after heating to 600^{O}C. The behaviour of the ammonium bicarbonate-precipitated product (ARZr7) is intermediate between that of ARZr2 and ARZr4, 30% weight loss being achieved by about 350^{O}C but with a significant change in the rate of weight loss between 150-350^{O}C.

The DTG curves shown in Fig. 6 (b) illustrate these differences more clearly. Thus the DTG curve for ARZr4 exhibits a sharp maximum at approximately 100^{O}C, the most probably temperature for the loss of adsorbed water. This is in agreement with the observations of other workers (ref. 29 - 31). In contrast, the curve for ARZr2 is much more complicated, consisting of an initial but smaller peak with a maximum at about 100^{O}C, probably due to the loss of adsorbed water as for the ammonia-precipitated gel ARZr4 and a subsequent peak at 300-350^{O}C.

The nature of the carrier gas has a considerable influence on the final weight loss sustained by a given sample, as illustrated by the results in Table 1 for ARZr7 and for various ammonia-precipitated gels.

The existence in zirconia gels of a species that produces carbon dioxide on heating and is prepared using sodium bicarbonate as a precipitant has been demonstrated by EGA (ref. 11, 23) by chromatographic and gravimetric methods. Contents of carrier gases passed over sample ARZr2 heated to various temperatures and analyzed by chromatographic and gravimetric methods (ref. 11, 23) have shown that evolution of carbon dioxide commences at about 100^{O}C and reaches a maximum at about 300^{O}C (Fig. 7). Although the total amount of carbon dioxide evolved from the sample is relatively small ($\sim$ 3.5% of its total weight) its dissociation has a significant effect on the surface structure of the resulting solid (ref. 11). Taken in conjunction with the TG data these results point to the existence within the structure of ARZr2 of a small proportion of bidentate carbonato ligands that are disrupted only at relatively high temperatures.

The EGA 'spectrum' of sample ARZr5 (Fig. 8) obtained using the arrangement incorporating the detector of a gas chromatograph, shows a large desorption peak with a maximum at about 150^{O}C, corresponding to the loss of water and possibly some ammonia in good agreement with the thermogravimetric results obtained for sample ARZr4 (Fig. 6).

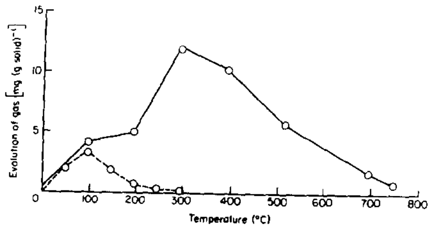


Fig. 7. Evolved gas analysis of various zirconia gel samples. — (a) Evolution of CO_2 gas from ARZr2; --- (b) evolution of NH_3 gas from ARZr6.

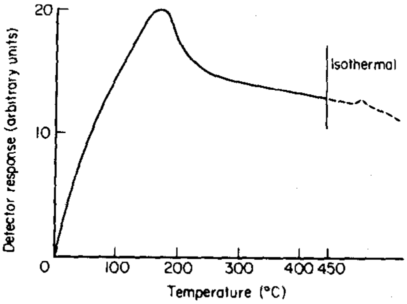


Fig. 8. EGA 'spectrum' for an ammonia precipitated gel sample ARZr5. The plot is isothermal above 450°C. Attenuator range of gas chromatograph: 16.

The DTA curves for zirconia gels exhibit an initial endothermic peak at about 170°C, corresponding to dehydration, followed by a strong sharp exothermic peak at about 430°C (the so-called 'glow phenomenon'), due to the amorphous to crystalline transition of ZrO_2 and Dollimore et al (ref. 32) have suggested the following scheme:

$ZrO_2 . xH_2O$
↓ 100°C
amorphous ZrO_2
↓ 300°C
metastable tetragonal ZrO_2
↓ 600°C - 650°C
tetragonal + monoclinic ZrO_2
↓ 800°C
monoclinic + (some tetragonal) ZrO_2

This scheme is however, an over-simplification of a more complex and variable series of transformations (ref. 11). Typical DTA curves obtained for the variously precipitated gels (Fig. 9) show that irrespective of the precipitant used the curves for all samples exhibit a number of common features. Thus they all exhibit a broad endothermic peak, commencing at 75 - 100°C and extending to 230 — 325°C, principally associated with the removal of water, and some also show the sharp exothermic peak that normally occurs at 470 ± 0.5°C. The existence of such an exothermic peak is a well documented feature of the DTA behaviour of many metal oxide and hydrous oxide systems (ref. 23) and has been referred to as a 'glow phenomenon'. However, in ascribing a fixed temperature to this phenomenon, previous workers have either

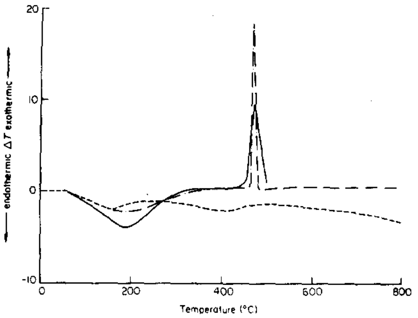


Fig. 9. Typical DTA curves for zirconia gels prepared with various precipitants. All samples prepared at pH7; curves measured in static air environment at heating rate of 10^{o}C min^{-1}. (a) --- ARZr2; (b) -.-. ARZr4; (c) —— ARZr7.

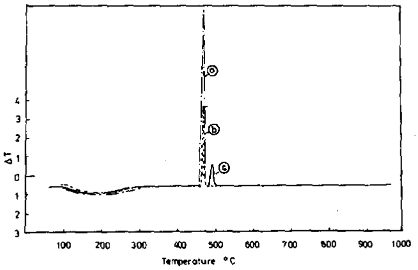


Fig. 10. The influence of environment on the glow exotherm of an ammonia-precipitated zirconia gel (ARZr5) -.-. (a) Static air; ---(b) nitrogen gas flow (100 cm min^{-1}) (c) hydrogen gas flow (100 cm min^{-1}); heating rate 6^{o}C min^{-1} in all cases.

been unaware of, or overlooked, the existence of other factors and conditions which influence its incidence. Thus, in addition to the nature of the precipitant, which clearly has an important influence on the magnitude of the glow exotherm (Fig. 9) the environment used during a particular DTA run is also important. A systematic study of this factor using the ammonia-precipitated gels yielded similar results for each sample, Fig. 10 being a composite plot of those pertaining to ARZr5.

X-ray diffraction and electron microscopic studies reveal that sodium bicarbonate product, although it shows no exotherm, has undergone crystallization (ref. 11, 23). Moreover, EGA and TG studies have shown that this gel evolves carbon dioxide around the temperature range of the glow exotherms. Thus, the endothermic effect of release of carbon dioxide apparently more than compensates the exothermic effect. Moreover, the amount of water present also affects the exotherm as shown by the better development of the exotherm for a wet sample in a flowing gas atmosphere (Fig. 11) and (ref. 11, 23). The magnitude and the temperature of the glow exotherm are also affected by prior thermal exposure. For example if a sample is heated to a temperature between 375^{o} and 450^{o}C and then held isothermally at that temperature, the glow exotherm appears; however, if the temperature is below 375^{o}C no glow exotherm is exhibited no matter how long the isothermal treatment is maintained.

The development of a mesopore system in the sodium bicarbonate precipitated gel can be directly related to the retention of small amount of CO_2 as a bidentate ligand in the structure of the gel. A combination of TG, EGA and DTA has succeeded in characterizing this evolved CO_2 and thus elucidating the origin and stability of mesoporosity in zirconia gels. The micropore volume in the ammonia products is essentially protected by water and some ammonia ligand (ref. 24) both of which are monodentate and hence more easily removed as revealed by thermoanalytical studies (ref. 11, 23). The removal of water and ammonia ligands is responsible for the collapse of the micropore structure by 200°C. (Fig. 2) and (ref. 22, 25). Ammonium bicarbonate precipitates would be expected to show the low-temperature microporosity of NH_3 products and high-temperature mesoporosity of the CO_2 ligands. A combination of surface chemical and thermochemical investigation (ref. 11, 22 - 25) demonstrated this to be true. Furthermore, the results obtained from surface characterization and thermoanalytical studies show that ligands derived from the various precipitants are incorporated in these gels and strongly influence their high-temperature behaviour. The observed properties are interpreted on the basis of a defect structure involving O^{2-} vacancies generated through the removal of these ligands at higher temperatures. The mechanism of this process has been detailed by Gimblett et al. (ref. 23).

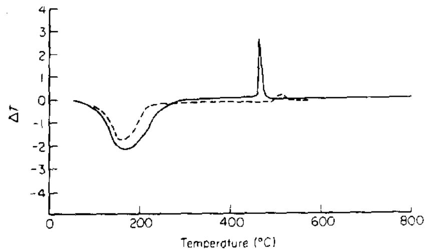


Fig. 11. The influence of water addition on the glow exotherm of a sodium bicarbonate precipitated zirconia gel (ARZr2). —— (a) Curve obtained in static air using a wet sample containing about 50% by weight of removable water; --- (b) curve obtained in dynamic hydrogen gas flow (100 cm min^{-1}) for a similar wet sample.

The above study reveals the value of thermoanalytical techniques in elucidating solid-state and surface-chemical properties of hydrous oxide systems. This approach has already been very useful in studies on chromia (ref. 27) as well as those on zirconia described above. Hence thermoanalytical techniques are likely to be applied increasingly in our efforts to understand the interdependence of the chemical history, the surface properties and the thermochemical behaviour of a wide range of hydrous oxide systems.

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