The preparation of group II oxide catalysts through acetate calcination: the influence of a support on the nature of the final catalyst.

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Abstract

The preparation of supported and unsupported group II oxide catalysts through oxidation of analogous group II acetates (Mg, Ca and Ba) in the presence and absence of a mesoporous silica material (SBA-15) was analysed using TGA. In the absence of the mesoporous support the acetates oxidised at different temperatures with a stability trend whereby Mg<Ca<Ba. The Mg and Ca salts were totally converted into the analogous oxides following treatment to 750°C (albeit with different routes of conversion) while $Ba(CH_3CO_2)_2$ was converted into $BaCO_3$.

Once dispersed onto SBA-15, all acetates combusted at similar temperatures irrespective of the counter-ion (indicating its nature was less important). The counter-ion also inverted the nature of the final material with, in this case, BaO and substantial amounts of CaO forming but $MgCO_3$ being the product of $Mg(CH_3CO_2)_2$ combustion.

Keywords: group II oxides, carbonates, SBA-15, catalyst characterisation

Introduction

Supported group II oxides have found application as catalysts in a wide range of processes including oxidative coupling of methane [1, 2], NO_x storage and release [3-6], O_2 and H_2 isotopic scrambling [7, 8] and, more recently, as solid basic catalysts in the promotion of the transesterification of triglycerides for the production of biodiesel [9, 10].

The nature of the oxide surface of these materials is obviously important with a range of surfaces being possible on the catalysts under working conditions. These range between hydroxylated surfaces, “clean” oxide surfaces, surfaces containing oxygen vacancies, surfaces covered with carbonate species and entire particles of group II oxides being in effect carbonate species *e.g.* see [11, 12].

Wet impregnation is one of the principal methods of preparation of supported group II oxides. This process involves the dispersion of a solution of an ionic precursor of the oxide onto a support surface followed by the removal of solvent and a high temperature calcination of the remaining solid mixture. When the counter-ion to the group II cation is an organic anion such as acetate, oxalate *etc*., this is lost to the atmosphere as CO_2 / H_2O upon combustion while the group II cation forms an oxide. The decomposition has also been reported to go through a carbonate intermediate species.

One of the, not unreasonable, assumptions of the wet impregnation process is that before calcination the deposited material exists as a spread of ions dispersed equally over the surface, and following calcination, a particle of supported species has formed.

The reaction between CO_2 and the group II oxide (especially in the presence of H_2O) can also lead to the formation of surface or bulk carbonates or bicarbonates. This process can take place as the catalyst is formed, or post-formation (from reaction in atmosphere) or during the catalysed reaction (if CO_2 is a reactant or product).

This contribution studies the conversion of group II acetate precursors into analogous oxides through temperature programmed oxidation in air. TGA is used to monitor changes in the masses of both unsupported and supported acetate salts as a function of temperature. The purpose of the experiments was to determine both the temperatures of acetate combustion and the nature of the material which remained following TGA, and also to study the effect that the presence of a solid support has on such transformations.

Experimental

Materials Mg, Ca and Ba acetate were purchased from Aldrich and were analysed for composition using elemental analysis prior to use. At the time of use it was found that the Mg salt was $Mg(CH_3CO_2)_2.⅓H_2O$, the Ca salt was $Ca(CH_3CO_2)_2.{}^2/_5H_2O$ and the Ba salt was anhydrous $Ba(CH_3CO_2)_2$.

Mesoporous SiO_2 synthesis In the cases where the acetates were supported on mesoporous SiO_2, SBA-15 was used. Numerous methods have been reported in the synthesis of SBA-15 and here we have adopted that first published by Zhao *et al.* in 1998 [13] and since widely cited. The reagents used were tetraethylorthosilicate (TEOS), pluronic 123 (P123), HCl and distilled water. 4g of P123 (0.00069 mol) was dissolved in 120 mL of 2M HCl (0.24 mol) and 30 mL of H_2O (7.85 mol) with stirring. Upon dissolution, the mixture was heated to 40 °C and 8.5 g of TEOS (0.0408 mol) was added. The solution (whose final molar composition was 1 TEOS : 0.00169 P123 : 5.88 HCl : 192 H_2O) was left stirring for 20 h. This then underwent an aging procedure under static conditions at 80 °C for a further 24 h. A white solid precipitate was filtered, washed with 2 L of distilled H_2O and dried in the oven at 80 °C overnight. This solid was calcined at 600 °C for 6 h. The BET surface area of these materials was ~ 650 $m^2\ g^{-1}$ and they had a measured pore size of ~ 10 nm.

To produce group II oxide loaded catalysts, these supports were dosed with appropriate masses of magnesium, calcium or barium acetate which had been dissolved in the required volumes of H_2O (where the required volume was the pore volume of 0.90 g of the mesoporous SiO_2). The eventual catalysts had mass loadings of 13.8% MgO, 10.6% CaO and 10.0% BaO. These materials were dried at 80 °C overnight prior to analysis with TGA.

Thermogravimetric Analysis.

TGA experiments, which were designed to mimic the calcination steps in supported and unsupported group II oxide catalyst preparation, were carried out in a Q500 TGA (TA Instruments) thermo-gravimetric balance. Prior to a TGA experiment, the empty pan was tared and loaded with 5 – 20 mg of the sample to be analysed. The sample was allowed to stabilise in an inert atmosphere (N_2) for 30 minutes. At the beginning of the temperature ramp, N_2 was replaced with a flow of air. The air line was fitted with a moisture / hydrocarbon trap and the nitrogen line with an oxygen / moisture / hydrocarbon trap. The balance was purged with 10 mL min^{-1} of N_2. The sample was held in a flow of 90 mL min^{-1} of air, while the temperature was increased from room temperature to 750 °C at a rate of 10 °C min^{-1}. In several cases complementary TPO_x experiments were carried out. In these instances, aliquots of the materials being analysed were held in a quartz reactor between two plugs of quartz wool and subjected to a flow of air at 90 mL min^{-1} and a portion of the exit gas was evacuated into a residual gas analysis mass spectrometer (Gaslab) where it was continuously analysed.

Results and discussion

Differential Thermogravimetric Analysis of acetate salts The DTGA profiles of unsupported Mg, Ca and Ba acetate is shown in Figure 1. The conversion of acetate to oxide can involve a carbonate intermediate, and indeed this is observed using the DTGA technique in some cases (see below).

At temperatures below 200 °C the removal of the water of hydration was noted from both the Ca and Mg salts. For these unsupported salts, the acetate species (and also any resulting carbonate species) decompose at higher temperatures as the atomic mass of the group II ion increases, *i.e.* Mg < Ca < Ba in terms of stability / resistance to oxidation.

The Mg acetate decomposition / oxidation begins at ~ 310 °C, that of Ca acetate at ~ 390 °C and that of Ba acetate begins at ~ 430 °C. This observation is in line with the proposal that the smaller the 2+ metal ion, the greater its charge density and therefore the greater its distortion effect on the negative acetate / carbonate species [14]. Secondary oxidation / decomposition peaks are present at 420 °C and 660 °C from magnesium acetate and calcium acetate respectively.

More information about the processes taking place can be gleaned through analysis of the actual mass losses associated with these DTGA peaks (see Table 1). Regarding the Mg acetate the overall mass loss at the completion of the experiment is that which would be expected following decomposition / oxidation of the acetate to form the oxide, *i.e.* (ignoring the water of crystallisation) there is a measured mass loss of 69%.

The first major peak in the DTGA profile represents the conversion of acetate to carbonate as well as the decomposition of a significant amount of carbonate to oxide. The expected mass loss following total conversion of acetate to carbonate would be ~41% while a mass loss of ~58% was observed during this event.

The mass loss associated with the second peak corresponds to the decomposition of the remaining carbonate to form oxide species. If the entire sample at this intermediate stage of the temperature ramp had been carbonate then a mass loss of 31% would be expected following decomposition to oxide while one of 11% was observed. Therefore, following the initial reaction event at 300 – 350 °C, approximately 63% of the Mg existed as MgO while the remainder was $MgCO_3$. The fact that we do see higher temperature carbonate decomposition is inconsistent with the findings of Niu *et al.* [15].

We can suggest two possible explanations for the apparently different stabilities of $MgCO_3$ and both rely on the different chemistries of the surface and bulk of $Mg(CH_3CO_2)_2$ particles. We envisage the material at the intermediate stage of the decomposition as being similar to a core shell $MgO/MgCO_3$ particle..

One possible explanation might relate to the stability of $MgCO_3$ on a MgO support, *i.e.* the surface $MgCO_3$ is more stable than that in the bulk. Therefore if the combustion proceeds acetate → carbonate → oxide, the latter remains on the material following the first event until it is decomposed at higher temperatures.

A second possible mechanism might involve the direct conversion of acetate to oxide followed by the trapping of the produced CO_2 (in the presence of H_2O) by Mg ions to form carbonate species at the surface layers of the particles.

In any case it is clear that, for a time during the TGA experiment, MgO and $MgCO_3$ co-exist within the material.

In the case of calcium acetate salt, these two reactions (conversion of acetate to carbonate and of carbonate to oxide) occur completely independently from one another. The lower temperature event ~ 390 – 430 °C represents the conversion of $Ca(CH_3CO_2)_2$ to $CaCO_3$ (a 35% mass loss) and the higher temperature event (between 600 – 710 °C) shows the mass loss corresponding to a $CaCO_3$ to CaO transformation (a further 27% mass loss). There is (within the margin of error of the technique) quantitative conversion of the Ca acetate to Ca carbonate during the first process and decomposition of the latter during the second event.

This mode of oxidation / decomposition is also true for barium acetate. In this case the carbonate is even more stable and the only mass loss evidenced before 750 °C is exclusively due to acetate conversion to carbonate. On completion of this experiment the Ba exists as solely $BaCO_3$ (with a mass loss of 23% associated with the single 430 – 480 °C reaction event). Our experiments were only carried out to 750 °C and the absence of a barium carbonate decomposition peak implies that higher temperatures are required to decompose the carbonates of this unsupported salt – this is in line with previously published results [14]. We did not note the formation of an oxalate intermediate as had been proposed by Hwang *et al.* [16].

TGA of calcined SBA-15 supported acetate salts

Significantly different profiles are noted when the acetate salts are dispersed by wet impregnation onto SBA-15 prior to the temperature ramp (see Figure 2). It should be noted that when SBA-15 is subjected to a temperature ramp under similar conditions to these (in the absence of metal acetate loading), water desorption is seen at temperatures up to ~150 °C. There is negligible mass loss observed thereafter between temperatures of 200 °C and 750 °C and therefore all the mass loss seen at these temperatures in the reported experiments can be ascribed to the oxidation and decomposition of the acetate species. Furthermore the overall mass loss here is significantly smaller than when the pure metal oxides are considered. This leads to less defined DTGA peaks.

In the presence of the dispersed acetate salts, desorption of H_2O is again seen at lower temperatures. This relates to the presence of water remaining on the catalysts following the drying step of the wet impregnation. A second feature common to all three materials is a reaction event centred between 400 and 450 °C. In complementary TPO_x experiments these features were shown to relate to the formation and release of CO_2 and H_2O (results not shown).

Comparison between Figure 2 and Figure 1 shows that the temperatures required for acetate combustion are now much closer to one another but that the trend in stability is reversed (*i.e.* for the temperature of maximum reaction Ba<Ca<Mg). $Mg(CH_3CO_2)_2$ has been somewhat stabilized by deposition onto the SBA-15 while conversely, $Ba(CH_3CO_2)_2$ has been somewhat destabilized. The temperature required for combustion of $Ca(CH_3CO_2)_2$ is relatively unchanged by the presence of the support.

The fact that these events are so closely related in terms of the temperature required suggests that the acetate combustion event is no longer substantially controlled by the nature of the cation. This would be expected given that the material would no longer be present in a defined lattice but rather dispersed as more isolated species on the SiO_2 surface.

An analysis of the extent of mass loss seen at temperatures above 200 °C, *i.e.* those relating only to the acetate combustion, also show some differences between the processes observed here and those seen in the case of the unsupported salt.

In the case of the combustion of supported $Mg(CH_3CO_2)_2$ only one broad mass loss peak is noted (between 300 and 500 °C). The mass loss observed during this event represents only the conversion of acetate to carbonate. There is no subsequent conversion of carbonate to oxide at temperatures below 750 °C.

Recall, in the case of the unsupported acetate, combustion to the oxide was complete by 450 °C (and significant amounts of oxide had been formed by temperatures of 350 °C). It is clear that when the salt is dispersed onto the SiO_2 support that both the Mg acetate and Mg carbonate are stabilized.

In the case of the supported $Ca(CH_3CO_2)_2$ material, the extent of acetate combustion is again different when the salt is the supported and unsupported. In the case of the combustion of supported $Ca(CH_3CO_2)_2$ the initial oxidation of acetate to carbonate is accompanied by some decomposition of carbonate to oxide.

For a sample of the given $Ca(CH_3CO_2)_2$ loading, the oxidation to carbonate should cause a mass loss of approx. 9% and the subsequent decomposition of the carbonate should cause a mass loss of another 8%. In fact 11% of the mass of the material is lost during the first step while a further 3% is lost during the second.

This indicates that (a) during the first step a significant amount of acetate is converted directly to carbonate or oxide and (b) an amount of carbonate remains undecomposed on completion of the experiment (note a total mass loss of ~ 14% when one of 17% would be expected).

Recall, in the case of the oxidation of the unsupported analogue, the oxidation of acetate to carbonate and the decomposition of carbonate to oxide were completely separate reaction events with their maximal activity at temperatures of ~420 °C and ~690 °C respectively.

Finally, for the oxidation of $Ba(CH_3CO_2)_2$ it is clear that there is also a difference between the cases of the reaction in the presence and absence of SiO_2. In the former case there was a quantitative conversion of $Ba(CH_3CO_2)_2$ to $BaCO_3$ in a reaction event that peaked at ~470 °C and no observed decomposition of the latter to temperatures of 750 °C. When supported $Ba(CH_3CO_2)_2$ is analysed in the same way the major mass loss peak is seen to reach a maximum at a temperature of ~ 410 °C. Analysis of the extent of mass loss associated with this peak confirm that it involves the complete conversion of $Ba(CH_3CO_2)_2$ to BaO, *i.e.* the oxidation of acetate and decomposition of any formed carbonate take place at the same time/temperature.

This is in marked contrast to the situation where Ba acetate alone is oxidised under the same conditions, *i.e.* a $BaCO_3$ species is formed and remains up to T = 750 °C. This result is in line with those discussed by Baiker *et al.* [14] who suggest that barium carbonates which form from acetate oxidation only require much increased temperatures to decompose when the barium loading is higher than 10%. In any case it is clear that the presence of SiO_2 has stabilized $MgCO_3$ and had an opposite effect on $BaCO_3$.

A rationale for the differences in the extents of formation of carbonate between the three samples in the supported catalysts might relate to the different atomic loadings. Each had a loading of between 10 and 13 wt % but this obviously translates into a greater concentration of surface Mg^{2+} cations compared with that of Ca^{2+}, and a lower again concentration of surface Ba^{2+} cations. If it is the case that surface carbonates form following the reaction between BaO and CO_2(g) then these reactions are far less likely to take place in the latter case (as the surface concentration of Ba^{2+} and of CO_2(g) would be far lower than the analogous concentrations of Mg^{2+} and CO_2(g) following acetate combustion of similar mass loadings of Mg acetate). Further studies looking at catalysts with similar mol% loadings would clarify this point.

Conclusions

The presence of the mesoporous SiO_2 affects the combustion of three group II oxides in that the trends in tendency towards oxidation are reversed. Mg>Ca>Ba in the unsupported case and Ba>Ca>Mg when the acetates are dispersed on SBA-15. Furthermore, there is an effect whereby the presence of the SiO_2 stabilizes carbonates of Mg and Ca which form following initial acetate oxidation while destabilizing carbonates on the Ba-containing material. Another possibility is that carbonates do not form on the supported Ba-containing material due to the relatively low concentrations of CO_2 and surface Ba^{2+} formed following initial acetate combustion on these particular samples.

Acknowledgements.

The UCD School of Chemistry and Chemical Biology is acknowledged and thanked for providing a studentship to LS. This contribution is dedicated to the memory of Prof. Joseph Cunningham, Department of Chemistry, UCC, Cork, Ireland.

References

[1] J. S. J. Hargreaves, G. J. Hutchings, R. W. Joyner and C. J. Kiely, Catalysis Today, 10, 259-265, 1991.

[2] J.H. Lunsford. Angwandte Chemie-International Edition in English, (1995), 34, 9, 970-980

[3] R. Burch, J.P. Breen, F.C. Meunier, Applied Catalysis B: Environmental (2002). 39, 4, 283-303.

[4] W.S. Epling, L.E. Campbell, A. Yezerets, N.W. Currier and J.E. Parks, Catalysis Reviews, Science and Engineering, (2004), 46, 2, 163-245

[5] Z.M. Liu and S.I. Woo, Catalysis Reviews, Science and Engineering, (2006), 48, 1, 43-89

[6] S. Royand A. Baiker, Chemical Reviews, (2009), 109, 9, 4054-4091

[7] J. Cuningham and C.P. Healy, J.Chem.Soc. Faraday Trans. I, (1987), 83, 9, 2973-2984

[8] J. Nunan, J.A.Cronin and J.Cunningham, J. Chem. Soc. Faraday Trans. I, (1985) 81, 2027-2041

[9] M. Lopez Granados, M.D. Zafra Poves, D.M. Martin Alonso, R. Mariscal, F. Cabello Galisteo, R. Moreno-Tost, J. Santamaria, J.L.G Fierro, Applied Catalysis B: Environmental, (2007), 73, 3-4, 317-326,

[10] M. Verziu, B. Cojocaru, J.C. Hu, R. Richards, C. Ciuculescu, P. Filip, V.I. Parvulescu, Green Chemistry, (2008), 10, 4, 373-381

[11] M.L. Bailly, C. Chizallet,G. Costentin, J.M. Krafft, H. Lauron-Pernot, H and M. Che, Journal of Catalysis, (2005), 235, 2, 413-422

[12] W.S. Epling, C. Peden, H.F. Charles and J. Szanyi, Journal of Physical Chemistry C, (2008), 112, 29, 10952-10959

[13] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka and G.D. Stucky, Science, (1998), 279, 548-552

[14] M. Piacentini, M. Maciejewski and A. Baiker, Applied Catalysis B: Environmental, (2005), 59, 187-195.

[15] S. Niu, K. Han, C. Lu and R. Sun, Applied Energy, (2010), 87, 2237-2242.

[16] U.-Y. Hwang, H.-S. Park and K.-K. Koo, Industrial & Engineering Chemistry Research, (2004), 43,728-734.

Tables and Figures

Figure 1

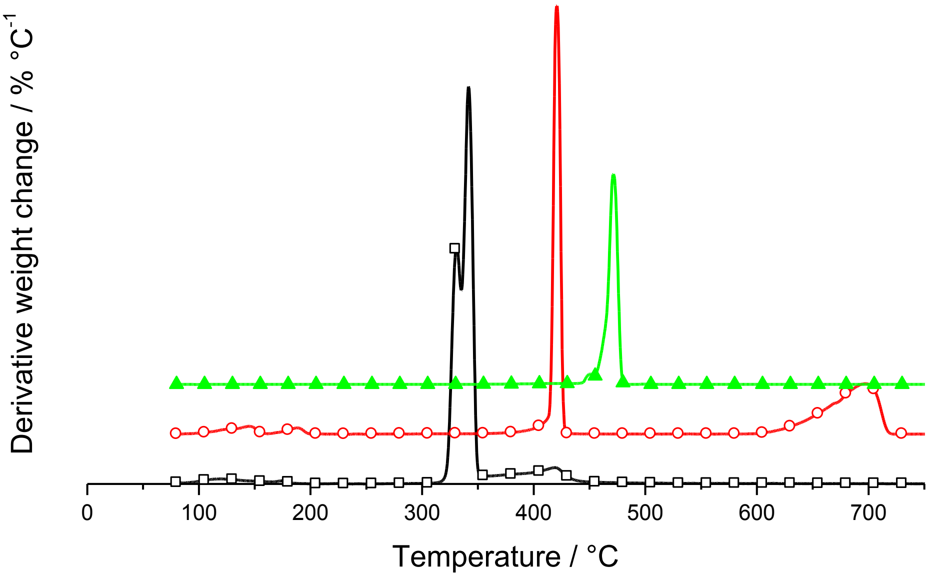

Figure 1 – Displaced DTGA profiles showing the oxidation / decomposition of Mg (□), Ca (❍) and Ba (▲) acetate.

Figure 2

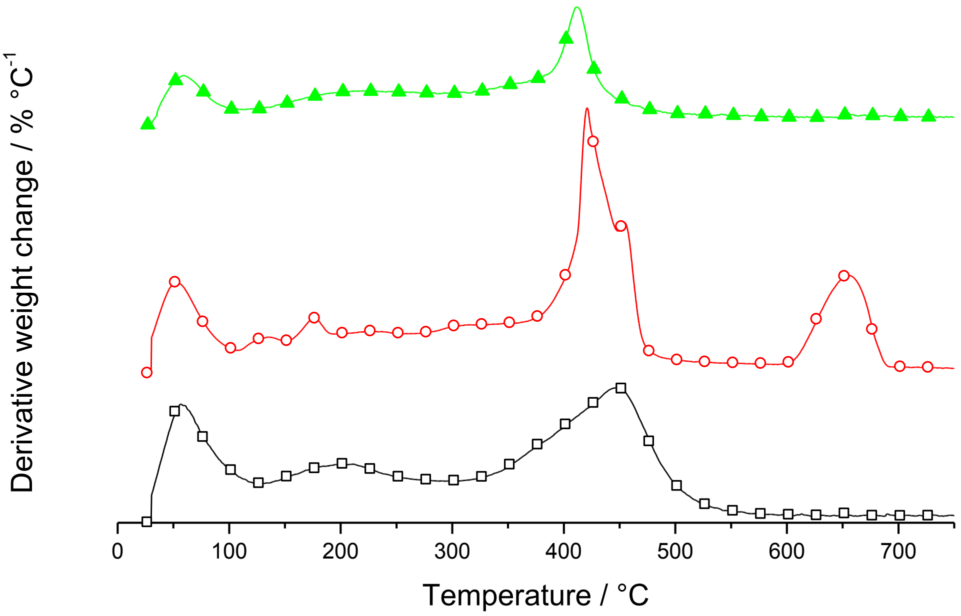

Figure 2. Displaced DTGA profiles from the oxidation of Mg (□), Ca (❍) and Ba (▲) acetate which had been dispersed onto the surface of pre-calcined SBA-15.

Table 1

	$T_{(max)}$ / °C	Observed % mass loss	Theoretical % mass loss, $(CH_3CO_2)_2^- \rightarrow CO_3^{2-}$	$T_{(max)}$ / °C	Observed %mass loss	Theoretical % mass loss, $CO_3^{2-} \rightarrow O^{2-}$
Mg	341	58	41	418	11	31
Ca	420	35	37	692	27	28
Ba	470	23	23	-	0	17

Table 1 – showing % mass loss associated with the profiles shown in Figure 1 and theoretical mass losses associated with acetate → carbonate and carbonate → oxide reactions (figures are rounded to the nearest %).

Table 2

	$T_{(max)}$ / °C	Observed % mass loss	Theoretical % mass loss, $(CH_3CO_2)_2^- \rightarrow CO_3^{2-}$	$T_{(max)}$ / °C	Observed %mass loss	Theoretical % mass loss, $CO_3^{2-} \rightarrow O^{2-}$
Mg	445	14	15	-	0	9
Ca	419	13	9	650	2	8
Ba	405	7	4	-	0	3

Table 2 – showing % observed mass loss associated with the profiles shown in Figure 2 and theoretical mass losses associated with acetate → carbonate and carbonate → oxide reactions for catalysts of the loadings discussed in the text (figures are rounded to the nearest %).