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Temperature-Dependent Dehydration of Sol–Gel-Derived Mullite Precursors: An FTIR Spectroscopic Study

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Abstract

Mullite type I precursors were prepared by a sol–gel process using tetraethoxysilane and aluminum sec.-butoxide as starting materials. The precursors were treated by 15 h heating steps in intervals of 100°C from 200 to 900°C and remain non-crystalline over the whole temperature range. The analytically determined water content of the preheated precursors decreases continuously with increasing preheating temperature. FTIR powder spectra of the preheated precursors show absorption bands in the region of the H_2O *and (Si,Al)–OH combination modes (5160 and 4540* cm^{-1}*), (*H_2O*, OH) stretching modes (3430* cm^{-1}*) and* H_2O *bending modes (1635* cm^{-1}*). FTIR results provide evidence for the presence of both* H_2O *molecules and OH groups in the precursor structure. In precursors preheated up to 600°C the* OH/H_2O *ratio increases continuously with increasing preheating temperature. Above 600°C, molecular* H_2O *is the dominating component of the precursors, indicating a recombination of OH groups to* H_2O *molecules. On the basis of wavenumber positions of the deconvoluted stretching mode bands, non-bridging and bridging* H_2O *molecules (3440 and 2961* cm^{-1}*) and OH groups (3585 and 3226* cm^{-1}*) are discerned. The formation of non-bridging* H_2O *represents an initial stage to the complete dehydration of the mullite precursor phases. On the basis of FTIR data a mechanism of precursor dehydration is developed: Up to about 400°C the molecular* H_2O *which adheres at the surface and in open pores of the precursor leaves the network by evaporation together with organic residuals. Above 600°C the thermal energy is high enough for dehydroxilation. The OH groups then recombine to molecular* H_2O*. Since dehydroxilation takes place in a temperature field of strong network condensation, part of the 'recombination-produced'* H_2O *is trapped in newly formed closed pores, giving rise to a relative increase of molecular* H_2O*. The high vapour pressure of the entrapped* H_2O *above about 800°C causes microfracturing of the precursors. Along the formed microcracks* H_2O *rapidly evaporates, leaving behind nearly water-free precursors at 900°C. © 1998 Elsevier Science Limited. All rights reserved*

1 Introduction

Mullite is one of the most important compounds in the ceramic industry. Due to its excellent thermomechanical properties, mullite has gained great significance as an engineering material for structural and functional ceramics. For advanced applications, especially in the field of optics and electronics, the synthesis of high-purity and ultrafine mullite precursor powders is of increasing importance.[1,2] A convenient method for the synthesis of the precursor powders is sol–gel processing. Phase development and thermal behaviour of the sol–gel derived mullite precursors show considerable differences, which depend on the reaction conditions during synthesis and the nature of the starting materials, both controlling the mixing level of Al and Si within the precursors.[3] Since the crystallization paths of the precursor powders significantly influence the properties of the final ceramics, detailed knowledge on the temperature-dependent structural development of the mullite precursors is of importance.

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Three main types of mullite formation processes in precursors for stoichiometric ($3Al_2O_3 \cdot 2SiO_2$) mullite compositions are described.[4] All precursor types are synthesized by sol–gel routes using admixtures of tetraethoxysilane (TEOS) and aluminum sec.-butoxide [$Al(OBu^s)_3$] as starting materials. Type I mullite precursors are produced by slow hydrolysis with very small amounts of H_2O, type II precursors by rapid hydrolysis with excess H_2O at strongly basic pH conditions ($pH > 10$), and type III precursors with excess H_2O at moderately basic pH conditions ($pH < 10$). From room temperature up to 900°C, type I and type III precursors are non-crystalline. Above this temperature type I precursors crystallize to alumina-rich mullite, while type III precursor transforms to γ-Al_2O_3. In both cases a silica-rich amorphous phase is coexisting with the crystalline phases. Mullite formation in precursor type III starts at temperatures $\geq$1200°C. Type II precursors consist of a non-crystalline SiO_2-rich phase and poorly crystalline pseudo-boehmite, transforming to γ-Al_2O_3 at $\geq$350°C, while mullite crystallization occurs above 1200°C. The different phase formations above 900°C in type I and type III precursors have been explained with a different short-range atomic order below this temperature.

The aim of this paper is to provide a model for the temperature-dependent structural evolution of type I mullite precursors with special regard to the dehydration process, considering a better control of tailoring microstructures and properties of advanced mullite ceramics.

2 Sample Preparation and Experimental Procedure

The mullite precursor phase was prepared by using TEOS, $Si(OC_2H_5)_4$ (Merck, art. no. 800658) and $Al(OBu^s)_3$, $Al(OC_4H_9)_3$ (Merck, art. no. 820054) as starting materials, admixed and diluted with isopropanol. After homogenization the mixture was allowed to hydrolize only by air contact in a glove box (relative humidity ≈40 %). The duration of the hydrolysis process was 10 days. The resulting gel was dried at 150°C, separated and differently treated by 15 h heating steps at temperatures of 200, 300, 400, 500, 600, 700, 800, and 900°C. After the heat-treatment all samples were stored in a desiccator, in order to avoid absorption of atmospheric water. X-ray diffractometry performed with the Philips X'pert, proved all samples to be non-crystalline, also the precursor preheated at 900°C. The FTIR spectrum of the 900°C preheated precursor in the lattice vibration region resembles that of the 500, 600, 700 and 800°C preheated precursors and reveals no spectral features of a crystalline mullite phase. Powders of the samples were produced by dry short-time hand-grinding in an agate mortar.

The water content of the as-prepared (150°C dried) precursor and of the preheated precursor phases was determined with a modified Du Pont moisture evolution analyzer (MEA) 903 H, working on the basis of water electrolysis.[5] The water content of ultrapure $Mg(OH)_2$ (Merck, art. no. 5870) was used for standardization of the MEA. 3·7–5·1 mg of each preheated precursor sample were annealed at a rate of $500°C\,min^{-1}$ to 970°C and held at this maximum temperature for 60 min. The water evolved was taken as the total analytical H_2O^+ content of the precursor phases. The mean error of the values determined amounts to ±0·5 wt%.

For the weight-loss determinations a computer controlled Mettler thermobalance TG 50, based on a M 3 microbalance and equipped with a TA 4000 Thermo Analyses System was used. Each preheated precursor sample (17–24 mg) was annealed in a flowing nitrogen stream of $150\,cm^3\,N_2\,min^{-1}$ from a starting temperature of 30°C up to 1000°C at a heating rate of $5°C\,min^{-1}$.[6]

FTIR spectra were measured by means of the Perkin–Elmer FTIR spectrometer 1760 X equipped with a microfocus accessory. Because of the small amounts of samples available, and of a more effective sample handling with respect to a dry atmosphere, KBr micropellets were prepared for the investigations. A precursor powder/KBr weight ratio of 0·05 was used for the measurement of the H_2O and OH combination modes (5500–$4000\,cm^{-1}$ range) and a ratio of 0·0025 for the measurements in the (H_2O, OH) stretching and H_2O bending vibration region (4000–$1200\,cm^{-1}$ range). Great care was taken during sample preparation. Both powdered samples and KBr were dried at 110°C for 2 h and then pressed. The micropellets were kept in an oven at 110°C for 2 h prior to the measurements. Background and sample spectra were obtained from 64 scans each with a nominal resolution of $4\,cm^{-1}$. The data handling was managed by the program IRDM (Perkin–Elmer). The spectra in the (H_2O, OH) stretching vibration range were resolved into single Gauss-shaped absorption bands using the program PeakFit (Jandel Scientific). Three sets of FTIR measurements with preceding sample preparation were performed in order to minimize statistical errors.

3 Results

The analytical water contents determined by MEA are in good agreement with the thermo-gravimetrically determined weight-losses of the precursor phases preheated at temperatures above 400°C (Fig. 1). Significant differences in the water and weight-loss values (i.e. weight-loss values > MEA values) of the precursors preheated at lower temperatures are apparently due to the additional decomposition of the organic starting compounds.[2] A continuously decreasing analytical H_2O+ content is evident from Fig. 1. The water content of the precursor preheated at 200°C amounts to 22·5 wt%, at 700°C to 14·2 wt%, and the 900°C preheated precursor contains only 1·8 wt% H_2O^+.

FTIR powder spectra in the 5500–4000 cm^{-1} range of the as-prepared precursor and of the differently preheated precursor phases are shown in Fig. 2. Figure 3 shows the 4000–1200 cm^{-1} range of the as-prepared precursor, and the preheated precursors. The spectrum of the precursors in the region of the H_2O and (Si, Al)–OH combination modes and of the (H_2O, OH) stretching and H_2O bending modes consists of two weak bands centered at 5160 and 4540 cm^{-1}, one very strong and broad band at 3430 cm^{-1} and one distinct band at 1635 cm^{-1}.[7] The great difference of the band intensity ratios in the stretching and bending mode region (3430 and 1635 cm^{-1}) along with the presence of the combination bands (5160 and 4540 cm^{-1}) prove that water is present as both H_2O molecules and OH groups. Figure 4(a) shows the integral absorbances of the 5160 cm^{-1} H_2O combination band, measured over spectral background.[8] A practically continuous and strong decrease of the absorbance values of precursors preheated up to 600°C and an abrupt increase at 700°C are the characteristic features of this diagram. The equivalent diagram of the (Si,Al)–OH combination

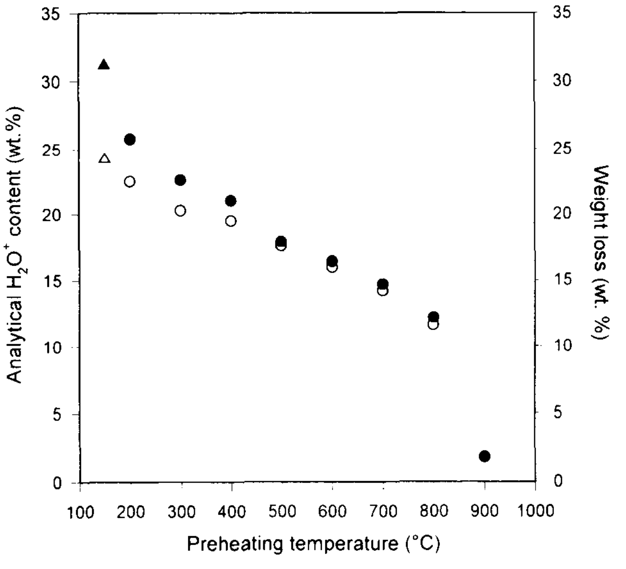

Fig. 1. Analytical H_2O^+ contents determined by MEA (open symbols) and weight losses determined by TG in wt% (full symbols) of the as-prepared (150°C dried) mullite precursor (symbol: triangles) and precursors preheated at temperatures from 200 to 900°C in intervals of 100°C (symbol: circles).

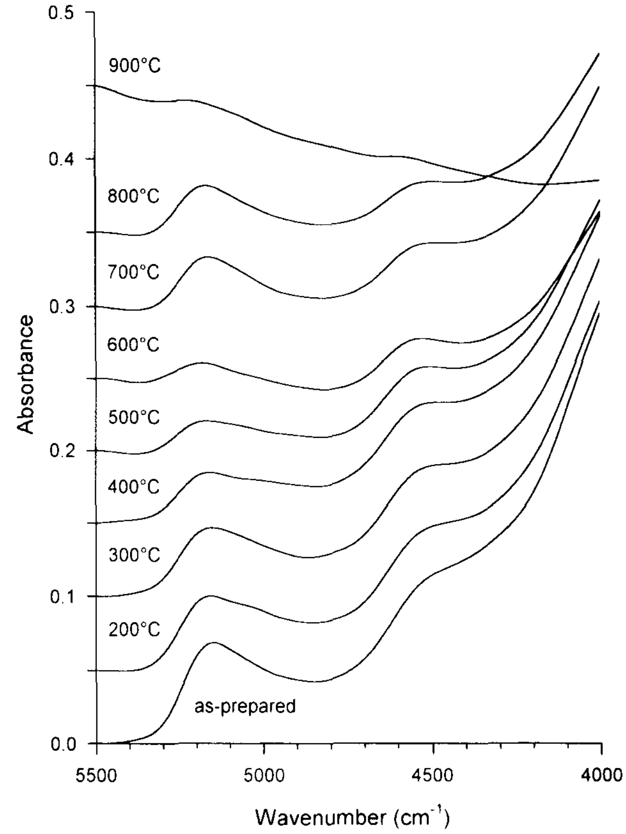

Fig. 2. FTIR powder spectra of the as-prepared mullite precursor and of the precursors preheated from 200 to 900°C in intervals of 100°C. The absorption band centered at 5160 cm^{-1} is due to the H_2O combination mode, the 4540 cm^{-1} band is due to the (Si, Al)–OH combination mode.

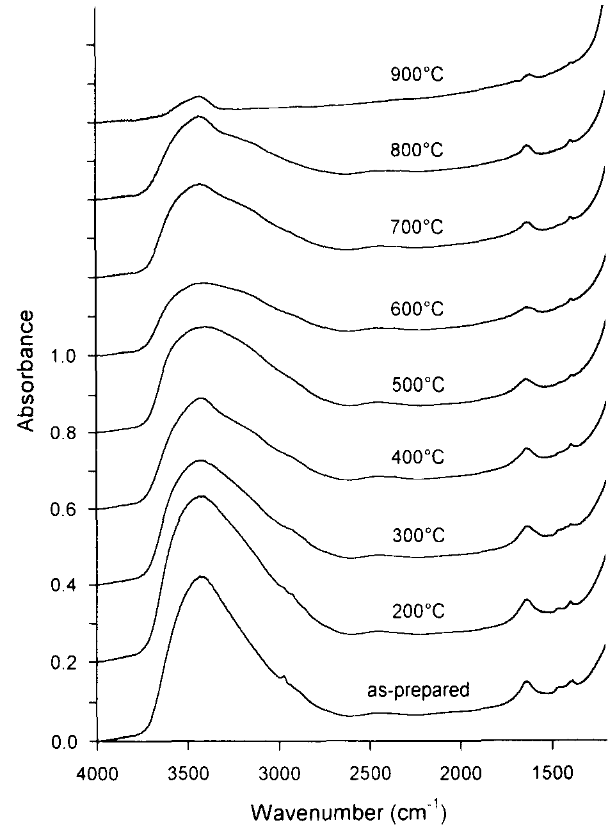

Fig. 3. FTIR powder spectra in the 4000–1200 cm^{-1} range comprising the absorptions due to the (H_2O, OH) stretching vibration centered at 3430 cm^{-1} and the H_2O bending vibration at 1635 cm^{-1} of the as-prepared mullite precursor and the preheated precursors.

band at 4540 cm^{-1} [Fig. 4(b)] shows slightly changing trends of absorbances up to 600°C, followed by an increasing negative slope for the precursors preheated at higher temperatures. Considering the continuous loss of the analytically determined total water content, this can be interpreted as a recombination of OH groups to H_2O molecules in precursors preheated at temperatures above 600°C. The absorbances of the H_2O bending vibration at 1635 cm^{-1} closely correlate to the absorbances of the H_2O combination modes, also confirming the discontinuity at 700°C. Under the reasonable assumption of similar molar absorptivities ε for the H_2O and OH combination modes,[7] a significant predominance of H_2O molecules over OH groups in the as-prepared precursor and in precursors preheated above 600°C is deduced. The assumption of somewhat different molar absorptivities ε for the H_2O and OH combination modes of the precursors preheated above 600°C results in a better coincidence of the strongly increasing H_2O absorbances in comparison with the relatively slight decrease of the corresponding OH absorbances. Preliminary measurements have shown that 15 min ball milling of the precursors in a micromill causes significant loss of water. In consequence of this observation, the sample powders used for the present study were produced by soft hand-grinding.

The strong and broad absorption band centered around 3430 cm^{-1} is due to stretching vibrations of H_2O molecules and OH groups. The integrated absorbance of this band is correlated to the water content determined by MEA; however, it also shows a slight discontinuity at 700°C, similar to that noticed in the H_2O combination and bending modes (Figs 2 and 3). Starting with reasonable wavenumber values, best observed as maxima and shoulders in the spectra of 'high-T pretreated' precursors, the deconvolution of the absorption in the stretching vibration region reveals four bands centered in the as-prepared precursor at 3585, 3440, 3226, and 2961 cm^{-1} (Fig. 5). These four bands (I–IV) are assigned to two different types of H_2O molecules and two different types of OH groups. Based on the observation that in the as-prepared and in the high-T precursors most of the water is present as H_2O, the strong band II at 3440 cm^{-1} is attributed to the stretching vibration of one type of H_2O molecules. This band is also dominating the absorption features of precursors preheated at 900°C. The significantly weaker band I at 3585 cm^{-1}, also present in the high-T precursors, is attributed to the stretching vibration of one type

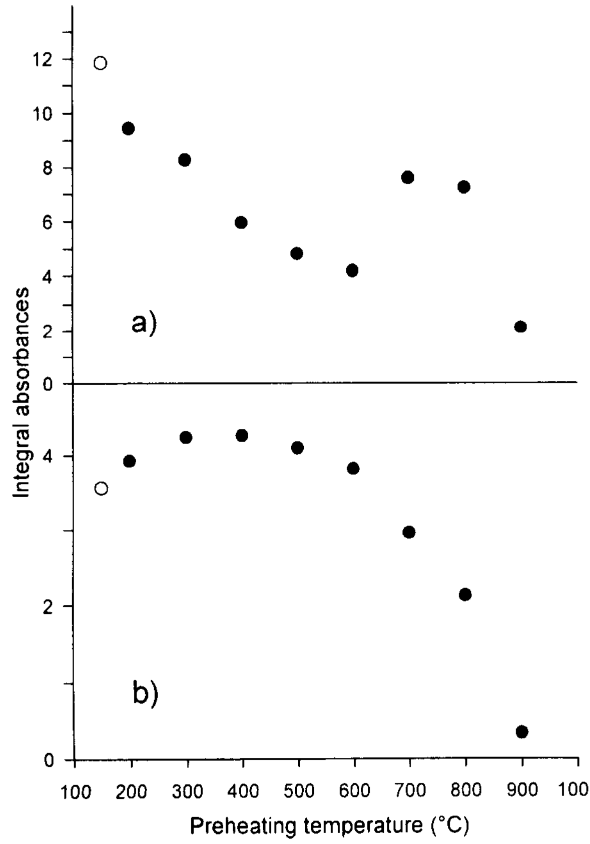

Fig. 4. Integral absorbance values of the as-prepared mullite precursor (symbol: open circle) and of the preheated precursors (symbol: full circles) a) of the H_2O combination band centered at 5160 cm^{-1}, b) of the (Si, Al)–OH combination band at 4540 cm^{-1}.

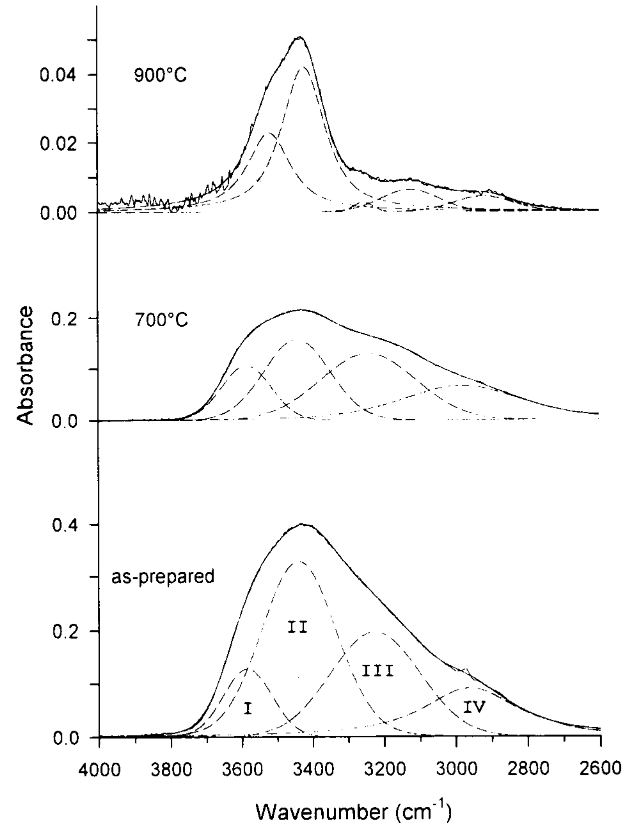

Fig. 5. FTIR spectra in the (H_2O, OH) stretching vibration region of the as-prepared mullite precursor and precursors preheated at 700 and 900°C. The spectra are resolved into single Gauss-shaped bands with maxima at 3585 (I), 3440 (II), 3226 (III), and 2961 m^{-1} (IV). Note the different absorbance scales.

of OH group. In precursor phases preheated at lower temperatures, H_2O and OH should be present in more or less comparable amounts, consequently the relatively strong band III at $3226\,cm^{-1}$ is attributed to a second type of OH and the weak band IV at $2961\,cm^{-1}$ to a second type of H_2O. Probably the band at $3440\,cm^{-1}$ is enhanced by the water content of the $Al(OBu^s)_3$ starting compound in the as-prepared precursor; the band III at $3226\,cm^{-1}$ may be influenced by the first overtone of the H_2O bending vibration. The bands generally follow the rule of a shift to lower wavenumbers with increasing temperature.[9]

4 Discussion

IR absorption bands due to the combination modes of H_2O molecules and OH groups prove the presence of both H_2O and OH in the precursor phases in similar amounts (Fig. 2). The relatively weak intensity of the H_2O bending vibration band compared to the strong band of the (H_2O, OH) stretching vibration, supports agreement with this observation (Fig. 3). The integral absorbance values of the combination modes show an increase of the OH/H_2O ratio up to 600°C [Fig. 4(a) and (b)]. At preheating temperatures above 600°C, molecular H_2O must be the dominating component, thus demanding a 'recombination-produced' H_2O. It is evident that the formation of H_2O molecules represents an initial stage to the complete dehydration of the mullite precursor phases. Despite the fact that the total amount of analytical H_2O^+ decreases continuously with increasing preheating temperature (Fig. 1), the integrated absorbance values of the overall (H_2O, OH) stretching vibration band centered at $3430\,cm^{-1}$ show a significant increase at 700°C (Fig. 3), which implies an argument for somewhat changing H_2O and OH absorptivities.

The deconvolution of the broad and strong absorption in the (H_2O, OH) stretching region reveals four bands attributed to two types of H_2O and two types of OH (Fig. 5). On the basis of the relation diagram given by,[10] bridging and nonbridging H_2O molecules and OH groups are discernable in the mullite precursor phases. The OH band position I at 3585 and the H_2O band position II at $3440\,cm^{-1}$ require practically no hydrogen bridging, whereas the OH band III at 3226 and the H_2O band IV at $2961\,cm^{-1}$ require strong hydrogen bonding with O–H...O distances of about 2·7 and 2·65 Å, respectively. A similar scheme of H_2O and OH bridging also exists in glasses; in addition to extremely short hydrogen bonds, strongly bonded and free H_2O molecules and OH groups are discerned.[11] The band assignment is also in agreement with the diagram of,[12] relating the band positions with the molar absorptivities. The spectra of precursors preheated at high temperatures are mainly determined by the band II at $3440\,cm^{-1}$ assigned to the stretching vibration of free H_2O. At preheating temperatures of 900°C, non-hydrogen bonded molecular H_2O and minor amounts of non-hydrogen bonded OH are the stable forms of water still present in significant amounts.

To date there exists no comprehensive model on the temperature-produced microstructural development of type I mullite precursors. We believe that the mechanisms discussed in Ref. 13 for SiO_2 gels may also apply in the present case. Using this model,[13] mullite type I precursors after drying are built up by clusters of a little branched network of low density. The clusters contain small nano-sized closed pores, whereas between the clusters relatively large open pore channels occur. After heat-treatment at 200°C the gel still has considerable amounts of organic residuals as well as non-bridging and bridging molecular H_2O and OH. While most of the molecular H_2O weakly adheres at the surface of clusters by van der Waals forces, the OH groups are much stronger structurally bound at the end of network branches. Up to about 400°C most of organic residuals decompose and evaporate together with the surface H_2O, while the firmly bound OH groups are more or less unaffected. In the IR spectrum this gives rise to a relative OH increase with respect to the total analytical H_2O^+ content determined by gravimetrical and electrochemical methods. At more elevated temperatures, between about 600 and 700°C the thermal energy is high enough for dehydroxilation of the precursor network and a subsequent recombination of OH to H_2O. Some of this 'recombination-produced' H_2O evaporates from the precursor, while another part is trapped in closed pores. H_2O trapping may be quite frequent because in the same temperature range strong and discontinuous condensation of the precursor takes place, producing a large number of closed micropores out of the formerly open pore channels. This interpretation is supported by the IR observation of a strong and discontinuous relative increase of molecular H_2O with respect to the total analytical H_2O^+ content in the same temperature field. With the amount of recombined H_2O and with temperature the vapour pressure of H_2O being entrapped in closed micropores does increase drastically. Above about 800°C this may induce microfracturing of the particulates, and as a consequence, enables H_2O to evaporate from the precursors' micropores. This process proceeds rapidly and at 900°C the precursor is nearly H_2O-free.

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