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Effects of water vapor on poly(vinyl butyral) ceramic binder burnout

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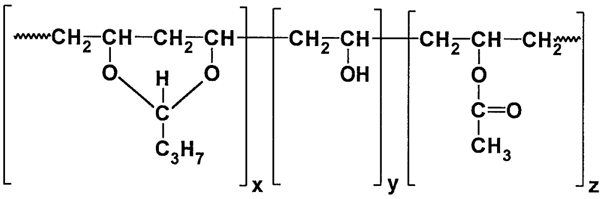
The effects of water vapor on non-oxidative poly(vinyl butyral) functional group decomposition mechanisms are described. Species-specific evolution profiles obtained by mass spectrometric analysis of gases evolved while heating silica, mullite, and α-alumina coated with poly(vinyl butyral) binder show that volatile product yields are affected by the presence of water vapor. When water vapor is incorporated into binder burnout atmospheres, acetic acid yields increase and C_4H_6O yields decrease. Acetic acid yields increased because water vapor interacted with oxide basic sites that otherwise reacted with acetic acid to form carboxylate species. Water vapor also inhibits C_4H_6O formation, possibly by stabilizing a polar intermediate produced during side group cleavage reactions.

1. Introduction

High-performance integrated circuits (IC) for use in new supercomputers must be high speed, have high wiring density, and be capable of rapid heat dissipation. Due to their low dielectric constants, low coefficients of thermal expansion, high thermal conductivities, high mechanical strengths, and relatively low fabrication costs, ceramics are preferred materials for construction of supercomputer IC chip packages [1, 2]. Ceramic IC chip packages are made by sintering stacked inorganic oxide greensheets in reductive atmospheres containing water vapor. Greensheets are composed of inorganic oxide powders (typically silica, alumina or mullite) held in place by a polymer binder. In addition, greensheets may contain small amounts of dispersing agents (e.g. poly(ethylene oxide)) and plasticizers (e.g. diisopropyl phthalic acid). Ideally, the thermal decomposition of the greensheet polymer binder, known as binder burnout [3, 4], should be completed during the early stages of sintering. Although complete binder burnout can usually be achieved by oxidative sintering, oxidative atmospheres cannot be employed for the production of ceramic IC chip packages because cofired metals used for circuit connections would be lost. When reductive atmospheres are employed for sintering, binder burnout must occur by non-oxidative mechanisms that often produce carbonaceous residue that remains on inorganic oxides and can result in flaws in ceramic products. By incorporating water vapor in sintering atmospheres, this residue can be removed by the water-gas reaction:

$$C + H_2O \leftrightharpoons CO + H_2$$

At ambient pressures, this reaction occurs above 900°C for graphite [5, 6], but the presence of inorganic oxides lowers reaction temperatures to 600–800°C [7]. Although the effects of the water-gas reaction on ceramic product quality have been studied, little is known about the effects of water vapor on binder burnout mechanisms. The effects of water vapor on the thermal decomposition of poly(vinyl butyral) (PVB) coated on silica, mullite, and α-alumina are described here. Commercial grade PVB is a multi-functional polymer that contains residual acetate ($z \sim 3\%$) and hydroxyl ($y \sim 20\%$) functionalities in addition to butyral ring structures.



PVB was selected for study because it is commonly employed as a greensheet binder for manufacture of ceramic IC chip packages and its non-oxidative binder burnout mechanisms have been thoroughly studied [7–12].

2. Experimental

The effects of water vapor on PVB binder burnout were investigated by using a Carbolite (Sheffield, England) 902PC tube furnace attached to a bubbler and operated by means of a Eurotherm (West Sussex, England) 902 temperature controller (Fig. 1). Sample temperatures were measured by a thermocouple located inside the furnace on which the sample holder was suspended. Water vapor was added to the binder burnout atmosphere by flowing helium through the bubbler shown in

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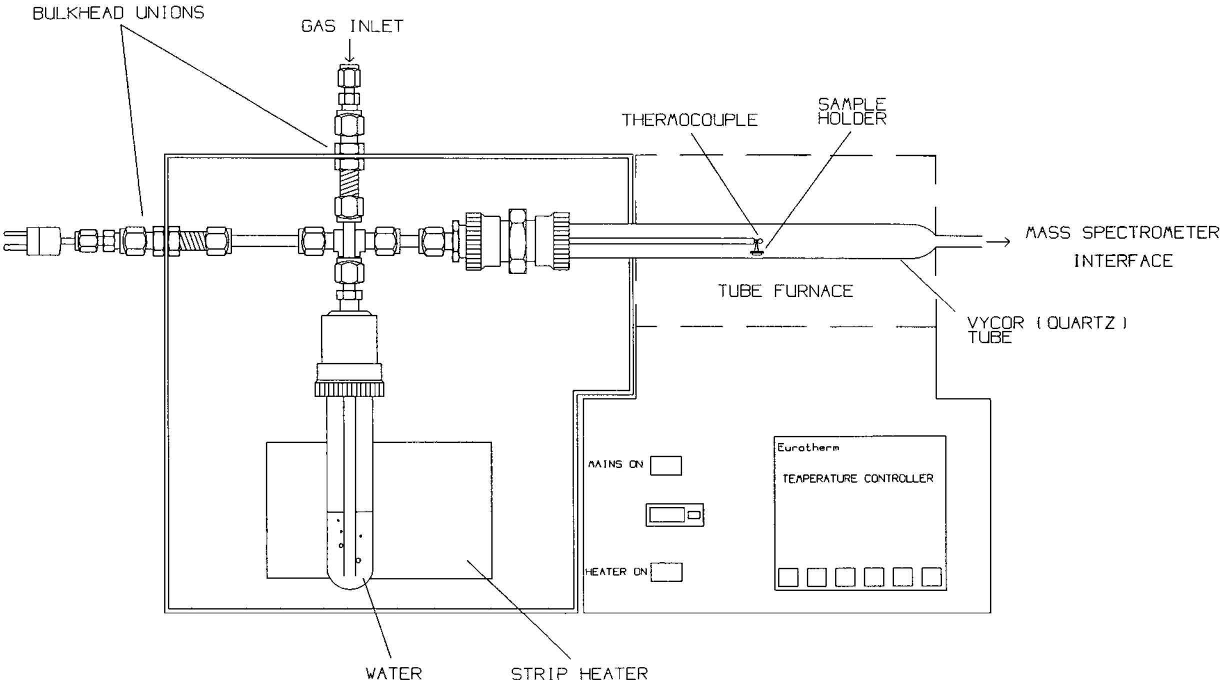


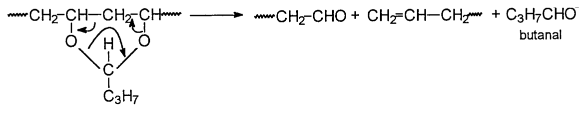
Figure 1 Apparatus employed for binder burnout studies.

Fig. 1. The water vapor content in the helium purge gas was adjusted to 90×10^{-3} kg/m^3 by setting the bubbler temperature to 50 °C. Approximately 20 mg samples were heated at a rate of 10 °C/min from 50 to 800 °C in helium flowing at a rate of 200×10^{-6} m^3/min. All analyses were performed in duplicate to confirm reproducibility. Mass spectra were acquired by diverting some of the furnace effluent through a heated interface and into a Hewlett Packard (Palo Alto, CA) 5985 quadrupole mass spectrometer, which was operated in electron impact mode with an ionizing voltage of 70 eV.

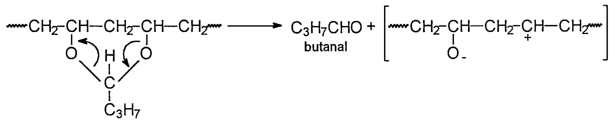
Silica, mullite, and commercial grade PVB (molecular weight $1.5\text{–}3.0 \times 10^5$) were obtained from Hitachi (Hitachi-shi, Japan). α-Alumina was purchased from Aldrich Chemical Co. (Milwaukee, WI). 1-Butanol was purchased from Omnisolv EM Science (Gibbstown, NJ). Helium (99.9995%) was purchased from Union Carbide Corp., Linde Division (Danbury, CT). Inorganic oxides were sieved prior to polymer/oxide sample preparation to restrict particle sizes to 63–150 μm. Inorganic oxide surface areas were 10, 2, and 0.7 m^2/g for silica, mullite, and α-alumina respectively. Inorganic oxide hydroxyl contents, measured by thermogravimetric weight loss, were 0.59, 0.48, and 0.33 weight percent for silica, mullite, and α-alumina respectively. Approximately 10% (w/w) PVB/oxide samples were prepared by dissolving 1.7 g of PVB in 250×10^{-6} m^3 of 1-butanol, adding 25×10^{-6} m^3 of this solution to 1.5 g of oxide, rotoevaporating the mixture to remove most of the solvent, and then drying overnight in an oven at 105–110 °C.

3. Results and discussion

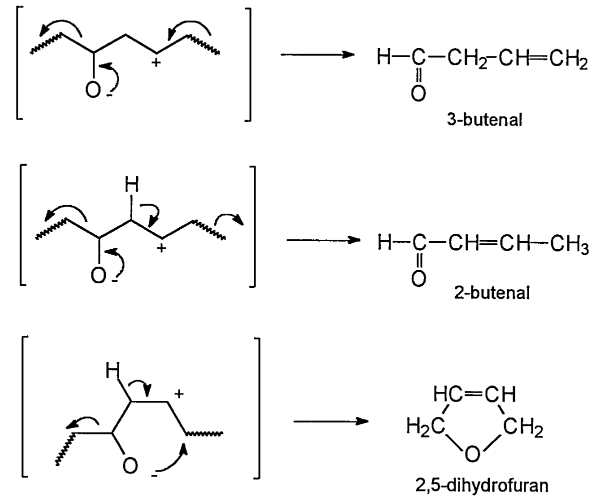
The quantities of oxidizable residue remaining after PVB/oxide binder burnouts in He were negligible compared to the volatile product yields. The white color of samples after studies in which water vapor was added to the purge gas indicated that the water gas reaction had removed the carbonaceous residue at 800°C. Consequently, evolution temperature profiles for PVB volatile decomposition products reflected the progress of temperature-dependent solid-state reactions. Previous pyrolysis gas chromatography/mass spectrometry (GC/MS) results from PVB binder burnout studies in the absence of water vapor revealed that the major volatile decomposition products from butyral rings were: butanal, butenal, and dihydrofuran [12, 13]. Thermal decomposition of polymer hydroxyl groups yielded water whereas acetate functionality decomposition resulted in acetic acid [12]. An intramolecular elimination mechanism has been proposed for the formation of butanal from PVB butyral rings [14]:



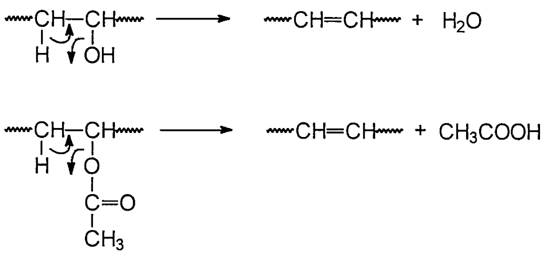
This process leaves aldehyde groups and chain end unsaturation in the polymer residue. Similarly, it has been proposed that butyral rings decompose via a side group cleavage mechanism [13]:



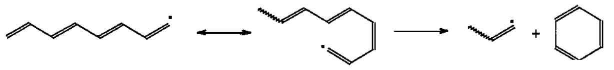
Like the intramolecular butanal elimination mechanism, chain end unsaturation and aldehyde groups can be formed by rearrangement of the side group elimination residue intermediate. In addition, C_4H_6O species such as butenal and 2,5-dihydrofuran can be formed:



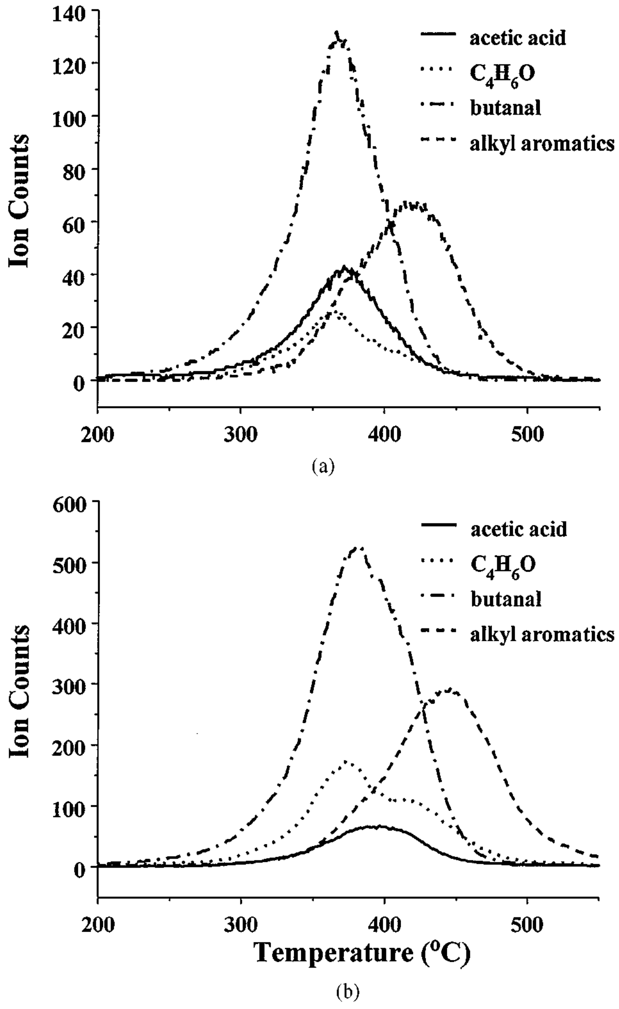
Water and acetic acid are produced from PVB hydroxyl and acetate functionalities by elimination processes [12, 15]:



Elimination processes create polyene segments that subsequently form aromatics at higher temperatures by free radical mechanisms [11]:



Our previous studies confirmed that the molecular ions for water (mass/charge ratio m/z 18), acetic acid (m/z 60), and butanal (m/z 72) could be monitored by evolved gas mass spectrometric analysis during binder burnout to provide species-specific evolution profiles [12]. In addition, m/z 91, which represents the tropylium ion, is species-specific for volatile alkyl aromatics. Unfortunately, species-specific ions for 2-butenal, 3-butenal and 2,5-dihydrofuran were not found. However, m/z 70, which is the molecular ion for all of these C_4H_6O species, was found to be specific for this group of substances. Evolution profiles for volatiles produced by heating PVB/oxide samples were obtained by plotting species-specific ion signals as a function of sample temperature. When water vapor was added to the helium purge gas, evolution profiles representing PVB hydroxyl dehydration could not be obtained because of the large m/z 18 background ion signal from the added water vapor. Consequently, the effects of water vapor on PVB dehydration were not examined in this study.



(a)

(b)

Figure 2 Species-specific evolution profiles obtained for the PVB/silica sample (a) with and (b) without water vapor in the purge gas.

Fig. 2 compares the species-specific ion signal temperature profiles for the PVB/silica sample in the absence and presence of water vapor in the helium purge gas. Each line represents the abundance of a species-specific ion detected by the mass spectrometer while the sample was heated. The butanal and C_4H_6O evolution profiles consisted of overlapping contributions and were more symmetric when water vapor was in the purge gas. Butanal and C_4H_6O ion counts were substantially diminished above 400 °C when water vapor was present, suggesting that water vapor facilitated low temperature decomposition processes. The ion signal temperature profiles in Fig. 2 also show that the relative yield of acetic acid increased and the temperature corresponding to the maximum acetic acid evolution rate decreased by about 25 °C when water vapor was added to the purge gas. The alkyl aromatics relative yield appeared to change little as a result of adding water vapor. Fig. 3 compares the species-specific ion signal temperature profiles for the PVB/mullite sample in the absence and presence of water vapor in the helium purge gas. Compared to the PVB/silica sample profiles, evolution rate maxima for the PVB/mullite sample occurred about 50 °C lower, which is consistent with previously reported results [12]. Like the PVB/silica sample, butanal and C_4H_6O evolutions for the PVB/mullite sample consisted of overlapping components. In contrast to the effects of water vapor on PVB/silica evolution profiles, the presence of water vapor caused all of the PVB/mullite species-specific profiles to broaden. Like the PVB/silica sample, the added water vapor

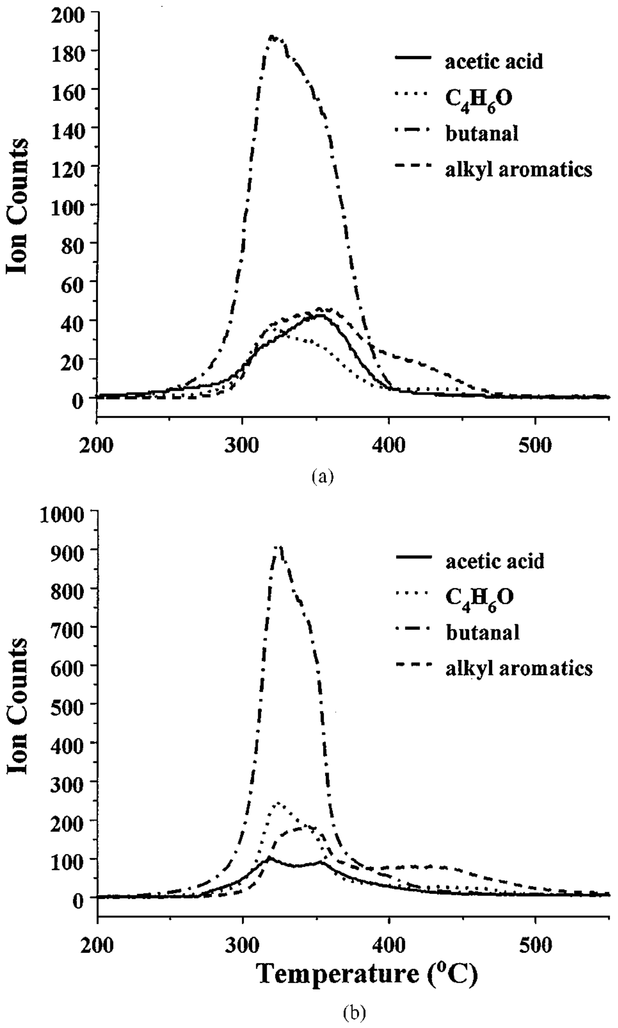


Figure 3 Species-specific evolution profiles obtained for the PVB/mullite sample (a) with and (b) without water vapor in the purge gas.

caused the relative yield of acetic acid to increase. Butanal and C_4H_6O relative yields decreased and the relative alkyl aromatics yield was essentially unchanged when water vapor was added to the purge gas. Fig. 4 compares the species-specific ion signal temperature profiles for the PVB/α-alumina sample in the absence and presence of water vapor in the helium purge gas. Species-specific evolution profile temperatures corresponding to maximum evolution rates for the PVB/α-alumina sample were similar to those measured for the PVB/silica sample. Butanal and C_4H_6O evolution profiles for the PVB/α-alumina sample contained at least two overlapping features. When water vapor was added to the purge gas, the low temperature component diminished. As for the other PVB/oxide samples, the addition of water vapor to the helium purge gas resulted in an increase in the acetic acid relative yield and the alkyl aromatics yield changed slightly.

Table I lists relative species-specific integrated ion signals derived from evolved gas mass spectrometric studies of heated neat PVB and the PVB/oxide samples in the absence and presence of water vapor in the purge gas. Relative yields listed in Table I represent the percentage of each species-specific integrated ion signal relative to the sum of all four integrated ion signals. Although these calculations do not provide mole percent or weight percent product yields, trends in the values listed in Table I are meaningful. Table I values are averages derived from two evolved gas analyses and were reproducible to within ±1 percent. Table I shows that the "relative" butanal yield was the largest for all samples and that none of the PVB/oxide samples yielded as much acetic acid as neat PVB. The C_4H_6O relative yield was much higher for the PVB/α-alumina sample than for the other samples. Conversely, the PVB/silica and PVB/mullite samples produced the highest relative yields of alkyl aromatics. For all of

TABLE I Relative species-specfic integrated ion signals (%)

	Evolved species			
Sample	Acetic acid	C_4H_6O	Butanal	Alkyl aromatics
Neat PVB	21	17	51	11
PVB/Silica w/o H_2O	8	16	51	25
PVB/Silica w H_2O	15	10	46	29
PVB/Mullite w/o H_2O	11	12	56	21
PVB/Mullite w H_2O	14	10	56	20
PVB/α-Alumina w/o H_2O	8	34	48	10
PVB/α-Alumina w H_2O	11	29	48	12

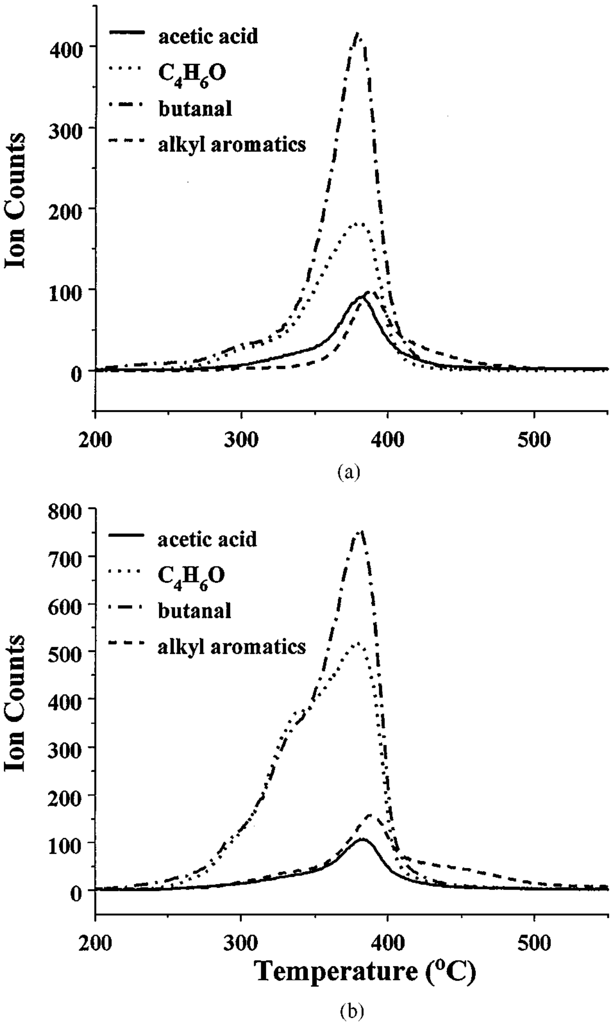


Figure 4 Species-specific evolution profiles obtained for the PVB/α-alumina sample (a) with and (b) without water vapor in the purge gas.

the PVB/oxide samples, the presence of water vapor in the helium purge gas resulted in increased acetic acid yields and decreased C_4H_6O yields. However, the decreased C_4H_6O yield for the PVB/mullite sample was not statistically significant when measurement error is considered.

Acetic acid formed by thermal decomposition of PVB acetate functionalities either evolved or reacted with oxides to form carboxylates [12]. At higher temperatures, adsorbed carboxylate species decomposed to form CO_2 [12]. Unfortunately, because of the small amount of CO_2 evolved by carboxylate decomposition and the CO_2 background in the mass spectrometer ion source due to small vacuum system leaks, it was not possible to detect carboxylate species decomposition by monitoring m/z 44 (i.e. CO_2 molecular ion). For all PVB/oxide samples, the relative yield of acetic acid increased when water vapor was present but did not reach the level detected for neat PVB. Water vapor likely occupied some of the oxide Lewis basic surface sites that reacted with acetic acid to form adsorbed carboxylate species. The acetic acid evolution profiles for the PVB/silica and PVB/α-alumina samples were symmetric, but the PVB/mullite sample acetic acid evolution profiles (Fig. 3) exhibit overlapping peaks that suggest that at least two reaction pathways were responsible for this product. Both of these evolution profile components occurred at temperatures below those for which acetic acid evolved from neat PVB, suggesting that mullite catalyzed acetic acid evolution at two different mullite surface sites. When water vapor was added to the purge gas, the high temperature acetic acid evolution was preferentially enhanced.

Several volatile products originated from PVB butyral ring decompositions. Previous studies have shown that thermal decomposition of PVB butyral rings leads mainly to the formation of butanal and C_4H_6O species [7–12]. Below 400 °C, the butanal and C_4H_6O evolution profiles for the PVB/silica sample (Fig. 2) maximized at about the same temperature, which would be expected if both species were produced by the same reaction mechanism (e.g. side group cleavage). However, the shape of the C_4H_6O evolution profile from the PVB/silica sample between 400 and 500 °C in the absence of water vapor does not correlate with the butanal evolution profile. This high temperature C_4H_6O evolution occurred at temperatures at which alkyl aromatics also evolved and likely resulted from residue cleavage near aldehyde functionalities that resulted from butanal intramolecular elimination reactions. Butanal and C_4H_6O evolution temperature profiles for the PVB/mullite and PVB/α-alumina samples (Figs 3 and 4) had similar shapes, again suggesting that C_4H_6O species were generated by mechanisms that also yielded butanal. However, the relative C_4H_6O yield was much greater for the PVB/α-alumina sample than for the others. The fact that butanal and C_4H_6O evolution profiles for the PVB/α-alumina sample consisted of overlapping features suggests that these species resulted from PVB interactions with at least two different α-alumina sites. The presence of water vapor greatly diminished the low temperature components of these evolution profiles. Although the evolution profiles for butanal and C_4H_6O were similar, the relative C_4H_6O yield decreased when water vapor was present whereas that for butanal was relatively unchanged (Table I). Thus, the presence of water vapor inhibited processes that yielded C_4H_6O but had little effect on butanal formation. Water would be expected to stabilize the polar side group cleavage intermediate, reducing the probability that C_4H_6O species would be evolved and increasing the likelihood that aldehyde groups and chain end unsaturation would form in the residue.

The proposed mechanism for the formation of alkyl aromatics during PVB binder burnout involves free radical cyclization of conjugated polyene segments in the polymer residue. These unsaturated segments arise from decomposition of PVB hydroxyl, acetate, and butyral ring functionalities. Consequently, the effects of water vapor on alkyl aromatics evolution depends on how the decomposition of the original functionalities were affected. All alkyl aromatics evolution profiles contained overlapping features. Low temperature alkyl aromatics evolutions occurred at temperatures at which butanal and C_4H_6O were also detected. The high temperature components of alkyl aromatics evolutions extended above temperatures at which butanal and C_4H_6O evolved and were derived from residue remaining after PVB functionalities had decomposed. Interestingly, added water vapor had little effect on the volatile alkyl aromatics evolution profile shapes. The changes in alkyl aromatics yields caused by added water vapor was statistically significant only for the PVB/silica sample. The fact that the PVB/α-alumina sample C_4H_6O yields were much higher and the alkyl aromatics yields were much lower than those for the other PVB/oxide samples is consistent with the assumption that these species arise from the same residue functionalities.

4. Conclusions

Although PVB binder burnout temperatures were primarily determined by the nature of the oxide on which PVB was coated, results described here clearly show that the presence of water vapor added to remove carbonaceous residue during ceramic sintering also affects the non- oxidative thermal decomposition of PVB binder. Depending on which oxide PVB was coated on, the effects of added water vapor on species-specific evolution profile shapes were different. However, for all of the PVB/oxide samples, added water vapor enhanced acetic acid relative yields and reduced C_4H_6O yields.

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