

Kinetic Investigation of ZrO₂, Y₂O₃, and Ni on Poly(vinyl butyral) Thermal Degradation Using Nonlinear Heating Functions

Leo Chau-Kuang Liao, Yu-Ching Chien

Department of Chemical Engineering and Materials Science, Yuan Ze University, Chung-Li 320, Taiwan

Received 25 November 2005; accepted 31 March 2006

DOI 10.1002/app.24683

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effects of zirconia (ZrO₂), yttria (Y₂O₃), and nickel (Ni) on poly(vinyl butyral) (PVB) thermal degradation were evaluated using kinetic analysis of TGA data and nonlinear heating rates. An exact solution derived from the Arrhenius equation in an integration form was used for the kinetic analysis. The kinetic parameters of the thermal degradation reaction were determined utilizing the solution and the isoconversional principle. Results show that the reaction pathway of the PVB thermal degradation was altered by the presence of these inorganic

materials except ZrO₂. The strong catalytic effects of Y₂O₃, and Ni on the PVB degradation were found and discussed according to the analytical results. The reaction rate was accelerated faster in lower temperatures in the presence of Y₂O₃, and Ni. The degradation period of the PVB/Ni sample appeared the shortest for these cases. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2552–2559, 2006

Key words: thermogravimetric analysis (TGA); kinetic analysis; ZrO₂; Y₂O₃; poly(vinyl butyral)

INTRODUCTION

Solid oxide fuel cells (SOFCs) are one of the high efficient devices to converse chemical fuel into electrical power. The general structure of the SOFC device consists of an anode, a cathode and an electrolyte in between. The major functions of the electrolyte perform as multiple purposes, such as a conductor of oxide ions (ionic conduction), leaking prevention, and thermal-shock resistance, in a high temperature operation around 600 to 1000°C. Therefore, the electrolyte performances are an essential part of the device to enhance the quality and efficiency for the use of the SOFCs.¹

The electrolyte properties are greatly affected by the material compositions and the fabrication process of this component. The component is made from ceramics, i.e., yttria-stabilized zirconia (YSZ), by sintering in high temperatures. Recently, the manufacturing of the electrolyte has been developed utilizing the microelectronic ceramic processing.[†] The beginning of the process is to prepare slurry by mixing the ceramics with solvents, powder dispersants, plasticizers and polymer binders. In the next step, green tapes of the ceramic components are formed on substrates to fabricate desired thickness or device

using a shape forming technique, such as tape-casting. The produced tapes are then to be sintered by a firing cycle of thermal treatments, including polymer binder burnout, ceramic sintering, and cooling steps.

In the binder burnout process, the polymer binders are decomposed into volatile products which evolve through the ceramic component above the decomposition temperatures. If a large amount of the evolving gas presents in the component, a high pressure buildup is generated to deform the ceramic body. Defects, such as cracking, blistering, and warping, may appear during the processing. Therefore, the removal of polymer binders plays an important role on defect formations of the components. Understanding the binder removal phenomena is a key issue to avoid defects and obtain better quality and higher yield of the products.²

Recent studies were focused on controlling the formation rate of the evolved gas (kinetics) with respect to the adopted heating strategy to avoid the forming of the pressure buildup inside ceramic components.^{3,4} The main theories of the pressure buildup to form the defects were proposed and focused on the kinetics of the evolving gas and the gas transport out of the ceramic body. Therefore, the fundamental knowledge of the degradation kinetics of binder removal corresponding to heating conditions has to be understood well to avoid the inappropriate operation.

In the microelectronic ceramic manufacturing, PVB is commonly used as a polymer binder for the fabrication of ceramic components, such as multilayer ceramic

Correspondence to: L. C.-K. Liao, (lckliao@saturn.yzu.edu.tw).

Contract grant sponsor: National Science Council, Taiwan, R.O.C; contract grant number: NSC94-2214-E-155-005.

capacitor (MLCC).⁵ This polymeric binder is a high adhesive agent to form flexible and high impact strength composites with ceramic materials. Kinetic analysis of thermal degradation of the PVB with inorganic materials has been investigated using analytical approaches. The effects of ceramics, such as glass ceramic, on PVB thermal degradation were studied in our previous work.⁶ The catalytic effects of the ceramics on PVB degradation were shown certain influences to accelerate the reaction rate in lower temperatures. These analytical data can be further applied to interpret and demonstrate the mechanism of PVB thermal degradation and binder removal process.⁷

In this work, kinetic analysis of thermal degradation of PVB with ZrO₂, Y₂O₃ (electrolyte), and Ni (anode) materials was carried out. The effects of these inorganic materials on PVB thermal degradation were evaluated by the proposed analytical algorithm. Parameters of the Arrhenius equation were determined and discussed to evaluate the kinetic effects for all these cases. The analytical data can be further used to the operation of the binder burnout process in our future studies.

KINETIC ANALYSIS METHOD

Kinetic equation of thermal decomposition of solid-state reaction is usually described by the Arrhenius equation as

$$\frac{d\alpha}{dt} = A \exp(-E_a/RT)f(\alpha) \quad (1)$$

where α is the conversion, t is the time, A is the frequency factor, E_a is the activation energy, T is the temperature, and $f(\alpha)$ is the reaction model.

If a heating rate, defined as $\beta = dT/dt$, is introduced into eq. (1), the equation can be modified as

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp(-E_a/RT)f(\alpha) \quad (2)$$

The heating rate is assumed as

$$1/\beta = C_0/T^2 \quad (3)$$

or in an integration form as

$$T = \frac{T_0}{\left(1 - \frac{tT_0}{C_0}\right)} \quad (4)$$

where C_0 is constant. The heating conditions for different C_0 are demonstrated in Figure 1. The integration form of eq. (2) can be expressed as

$$\ln[F(\alpha) - F(0)] = \ln \frac{AR}{E_a} + \ln C_0 - E_a/RT \quad (5)$$

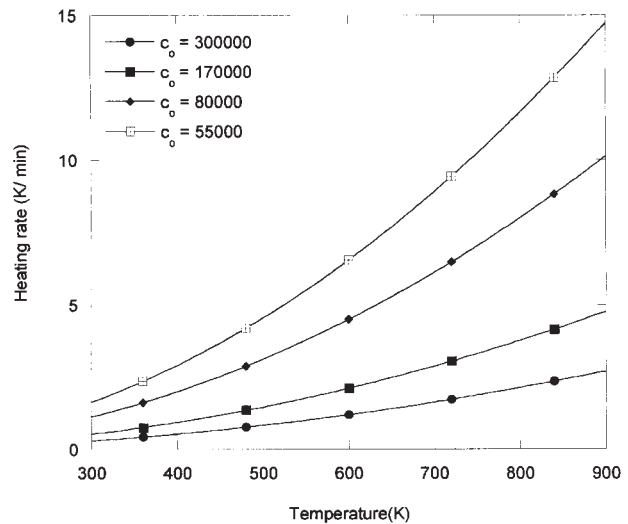


Figure 1 The heating conditions for different C_0 values.

If assume α is constant and differentiate eq. (6), then the equation becomes

$$\frac{d \ln C_0}{d(1/T)} = E_a/R \quad (6)$$

The frequency factor A can be determined by the following equation

$$\ln(A) = \ln \left\{ \frac{-1}{1-n} [(1-\alpha)^{1-n} - 1] \right\} \times \exp \left(\frac{E_a}{RT} \right) \times \frac{E_a}{RC_0} \quad (7)$$

for $n \neq 1$

and

$$\ln(A) = \ln \left\{ -\ln(1-\alpha) \times \exp \left(\frac{E_a}{RT} \right) \times \frac{E_a}{RC_0} \right\} \quad (8)$$

for $n = 1$

Detailed derivation can be found in our previous work.⁸ This algorithm shows more practical to analyze solid-state reaction using a set of different heating rates for determining the kinetic parameters.

EXPERIMENTAL

Commercial PVB sample (type B-90) provided by Monsanto Corp. was used in this study. The weight-average molecular weight is approximately 85,000 and its glass transition temperature is 74°C. The commercial ceramic and metal powders, ZrO₂, Y₂O₃, and Ni, which purity is greater than 99%, were obtained from Aldrich Corp. The average particle size is 12 μm for ZrO₂ and 2.5 μm for Y₂O₃. In addition, the water content is estimated as 0.18% and 0.15% for ZrO₂ and Y₂O₃, respectively.

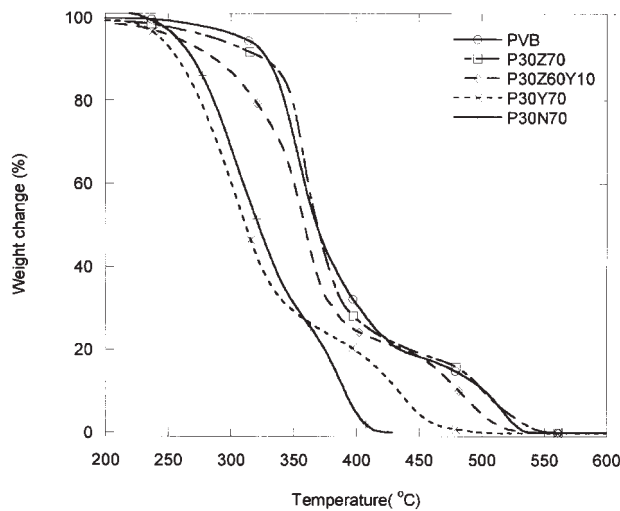


Figure 2 TG curves of thermal degradation of the composite samples at 10°C/min in air. (P30Z60Y10 denotes a composition of 30 wt % PVB with 60 wt % ZrO_2 , and 10 wt % Y_2O_3).

The analytical samples were prepared as two components of PVB powder mixing with each of the ceramic and metal based on the required composition. The samples were prepared and mixed fully by a Panasonic MX-T2GN powder mixer. The mixing operating parameters of the mixer were set up at 13,000 rpm for 3 min and repeated three times.

Thermogravimetric Analyzer (TGA) model Pyris 1 provided by Perkin–Elmer was used for the TG data collections and measurements. Before the experiments, TGA was calibrated by standard 100 mg platinum supplied by Perkin–Elmer. In addition, the temperature was calibrated by the Curie points of Ni and alloy

materials also provided by Perkin–Elmer. The sample weight and temperature can be well controlled and the furnace temperature of the TG could go up to 1300°C. About 10 mg of the sample weight was used in each experiment and the flow rate of the carrier gas was kept at 50 cm³/min. The TG can be programmable to be set up as a heating function and control the heating rates from 0.1 to 40°C/min. The sample weight change and temperature were recorded on a continuous basis.

RESULTS AND DISCUSSION

TG data analysis

The kinetic analysis of thermal oxidative degradation of PVB combined with ZrO_2 , Y_2O_3 , and Ni was carried out using TG data. The effects of these inorganic materials on PVB thermal oxidative degradation was discussed qualitatively and quantitatively. Figure 2 demonstrates that thermal oxidative degradation of PVB and PVB with these inorganic materials using TG measurements. The TG curves shows that the PVB degradation is much affected by the presence of Y_2O_3 and Ni. Moreover, the samples of PVB/ Y_2O_3 and PVB/Ni are degraded earlier in the beginning of the degradation at around 250°C. In the final degradation period, the residue of the PVB degradation is decomposed fastest for the PVB/Ni (P30N70) case. From the TG data analysis, the overall PVB degradation periods for the PVB/ Y_2O_3 and PVB/Ni cases are shorter than the one of PVB. Besides, there is apparently little influence of ZrO_2 on the PVB thermal degradation as illustrated from Figure 2. If a sample is prepared as PVB with both ZrO_2 and Y_2O_3 (P30Z60Y10), the weight change curve of this composite locates between the

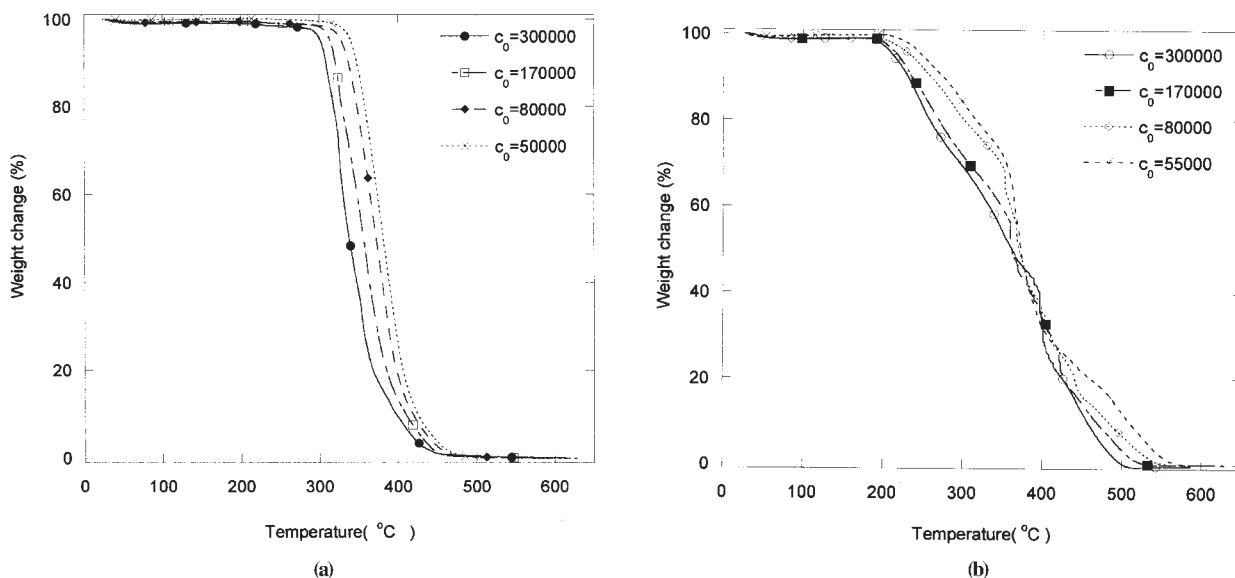


Figure 3 TG curves of thermal degradation of the P30Z70 case in different heating conditions in (a) nitrogen (b) air. (P30Z70 denotes a composition of 30 wt % PVB with 70 wt % ZrO_2).

curves of the P30Z70 and the P30Y70 cases as shown in Figure 2. This indicates that there is a dual effect of ZrO_2 and Y_2O_3 on the PVB thermal degradation.

The effects of these inorganic materials on the PVB degradation were investigated by a kinetic analysis using the nonlinear heating rate method. Figure 3 illustrates the weight change of the P30Z70 sample in nitrogen and air in different heating conditions. The weight change curves distribute smoothly for the sample in nitrogen in the heating conditions as shown in Figure 3(a); while in Figure 3(b), the curves intersect among the lines in the weight change ranges between 20 and 50% in air. This implies that the pathways of PVB degradation vary greatly in different atmospheres. Moreover, the degradation situation appears complicated from the TG measurements when operating in air.

The effects of Y_2O_3 , Ni and ZrO_2/Y_2O_3 on the PVB degradation in air are demonstrated in Figure 4 for the heating conditions. In Figure 4(a), the weight change curves of the P30Y70 sample distribute with intersecting among the curves between 40 and 20%, similar to those of the P30Z70 case. However, the curves change smoothly without any intersections and even in the final degradation period as shown in Figure 4(b). The degradation pathway for the P30N70 case seems quite different from both P30Z70 and P30Y70 cases. This result indicates that the PVB degradation mechanism is changed by the presence of Ni. The TG analysis of the P30Z60Y10 case was also carried out in Figure 4(c). Besides, the degradation conditions for these samples in nitrogen are quite similar to the result of the P30Z70 case in our observations.

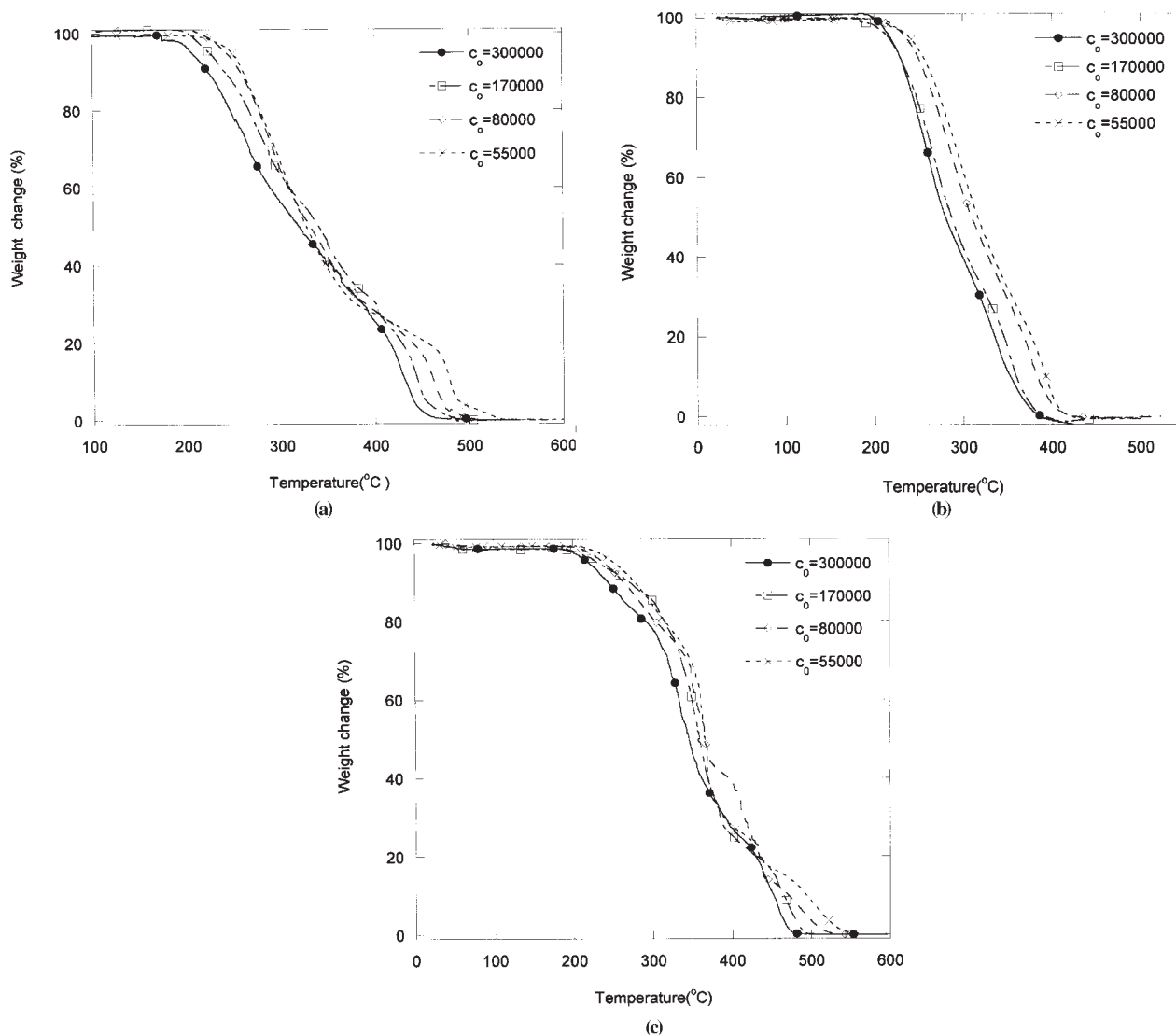


Figure 4 TG curves of thermal degradation of (a) P30Y70 (b) P30N70 (c) P30Z60Y10 samples in different heating conditions in air.

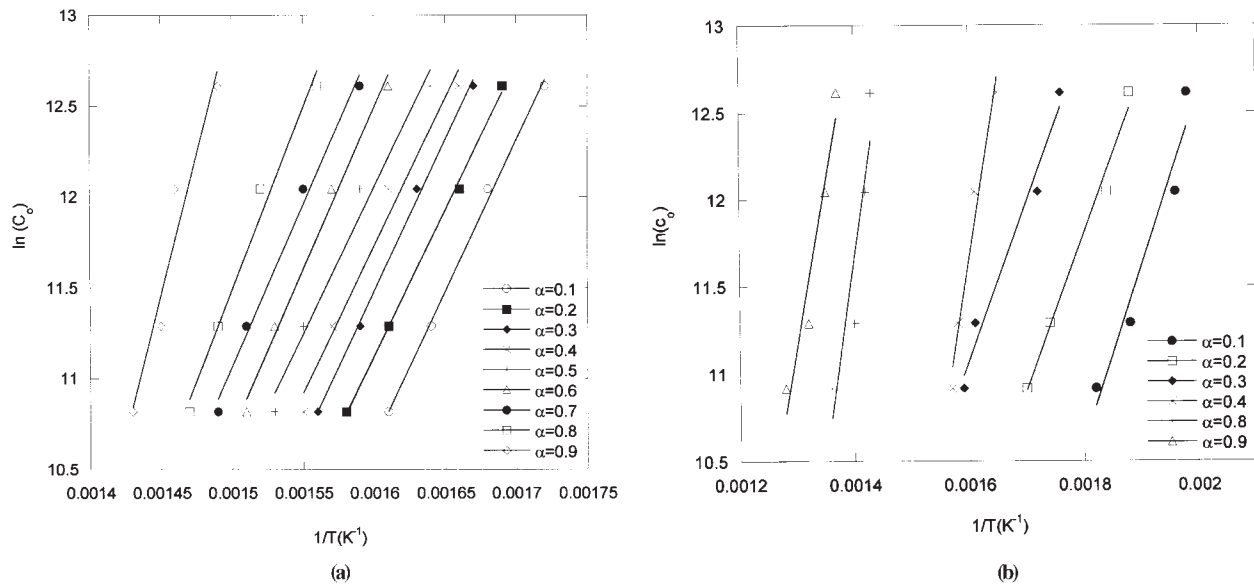


Figure 5 Plot of $\ln(c_0)$ versus $1/T$ transformed from the TG data to estimate the E_a values of the P30Z70 case in (a) nitrogen and (b) air.

Kinetic analysis

Kinetic analysis of the thermal degradation of the composite samples was carried out using the analytical approach described in the above section. Based on eq. (7), the activation energy (E_a) can be determined from the slope of $\ln(c_0)$ versus $1/T$. The thermal degradation of P30Z70 in nitrogen and air cases was

depicted as shown in Figure 5 corresponding to conversion. In Figure 5(b), the E_a values can be estimated except for the conversion between 0.5 and 0.7 due to the intersection of these curves. The intersection region represents that the residue left after the PVB degradation is not influenced by the heating conditions. Therefore, the E_a data can not be accurately calculated using the proposed analytical method in this

TABLE I
Data of Kinetic Parameters for Different Samples

(P30Z70) ^a									
α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
N_2									
E_a^b	138	134	138	134	134	148	148	167	256
$\ln(A)^c$	23.33	22.82	23.75	23.13	23.11	25.75	25.67	29.04	44.42
Air									
E_a^b	83	75	75	173	60	44	48	189	157
$\ln(A)^c$	14.36	11.96	11.50	30.88	8.16	4.70	5.62	30.77	24.03
(P30Y70) ^a									
α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
E_a^b	89	121	147	166	35	31	23	178	162
$\ln(A)^c$	16.01	23.29	28.79	32.06	3.27	2.43	0.68	29.03	25.78
(P30N70) ^a									
α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
E_a^b	114	123	117	117	117	124	131	131	131
$\ln(A)^c$	22.30	24.29	22.67	22.46	22.14	23.18	24.06	23.55	23.31
(P30Z60Y10) ^a									
α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
E_a^b	102	126	169	187	209	47	35	41	181
$\ln(A)^c$	18.41	22.54	30.51	33.67	37.82	5.57	3.08	4.23	28.32

^a P30Z70: 30 wt % PVB with 70 wt % ZrO_2 ; P30Y70: 30 wt % PVB with 70 wt % Y_2O_3 ; P30Ni70: 30 wt % PVB with 70 wt % Ni; P30Z60Y10: 30 wt % PVB with 60 wt % ZrO_2 and 10 wt % Y_2O_3 .

^b Activation energy (kJ/mole).

^c Arrhenius constant (min^{-1}).

region. An alternative way is to apply the following equation using in our previous studies^{6,7} as

$$\ln \left[\frac{F(\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta (E + 2RT)} \right] - \frac{E_a}{RT} \quad (9)$$

where $F(\alpha)$ is the integral form of the function $f(\alpha)$. A linear relation should be expected from the plot of $\ln[F(\alpha)/T^2]$ against $1/T$ and $-E_a/R$ value is the slope of the plot. The estimated kinetic parameters are listed in Table I. The E_a data are about 140 kJ/mol averagely in the nitrogen case, except in the final degradation period ($\alpha > 0.8$). However, the E_a values distribute and vary in a wider range with respect to the conver-

sion for the air case. This demonstrates that thermal degradation of the P30Z70 sample is more complicated in air than in nitrogen. In addition, there are probably several degradation periods when operating in air based on the E_a data analysis and the isoconversational theory.

The kinetic parameters of P30Y70, P30N70, and P30Z60Y10 cases were obtained using the same analytical approach. The plots of the data to determine the E_a values with respect to conversion for these cases are shown in Figure 6. The determined kinetic parameters were listed in Table I. Particularly, the distribution of the E_a values for the P30N70 case is quite uniform but different from the other cases. This verifies that the thermal effect of Ni on PVB degradation can greatly alter the reaction pathway

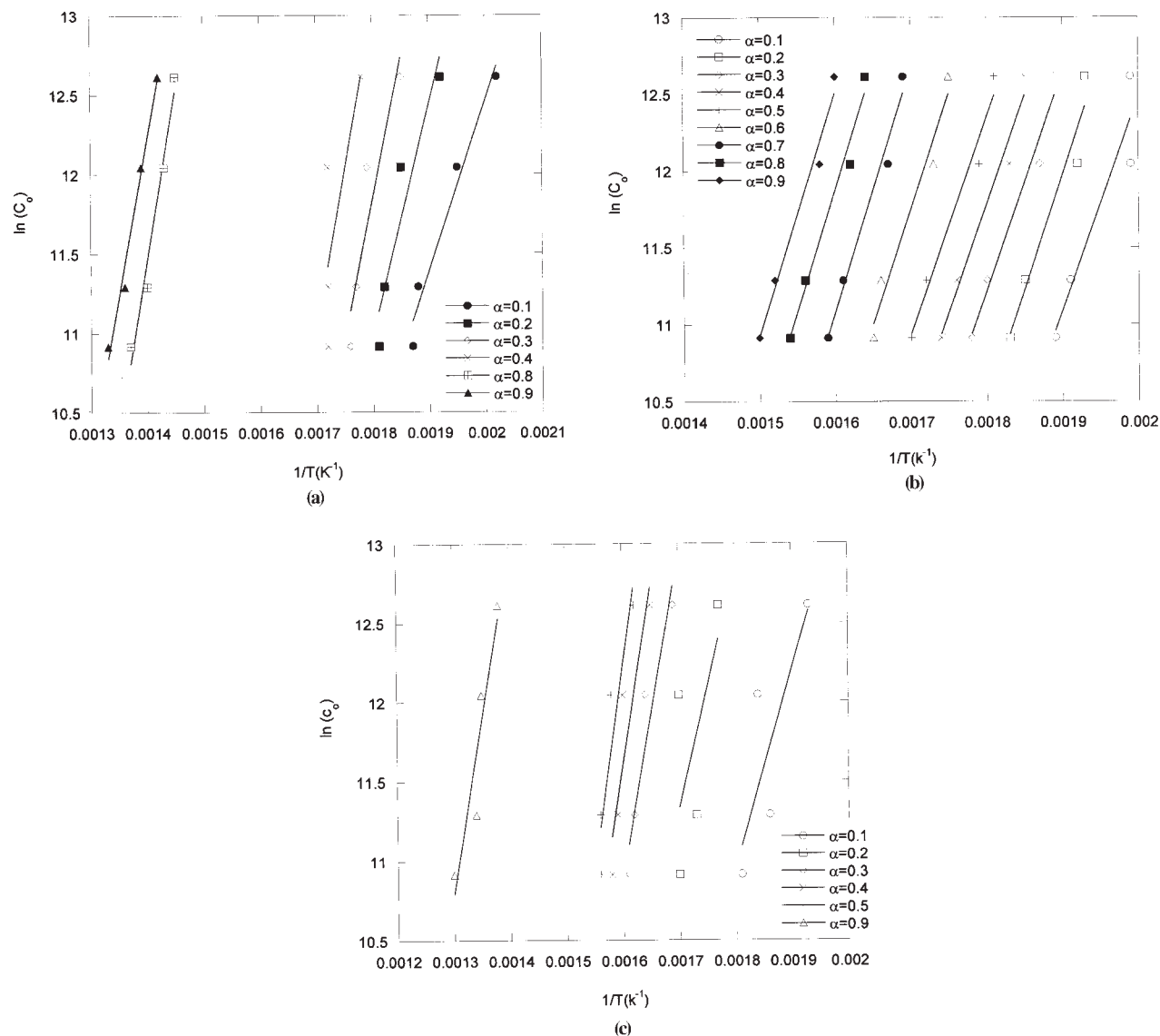


Figure 6 Plot of $\ln(C_0)$ versus $1/T$ transformed from the TG data to estimate the E_a values of the (a) P30Y70 (b) P30N70 (c) P30Z60Y10 cases.

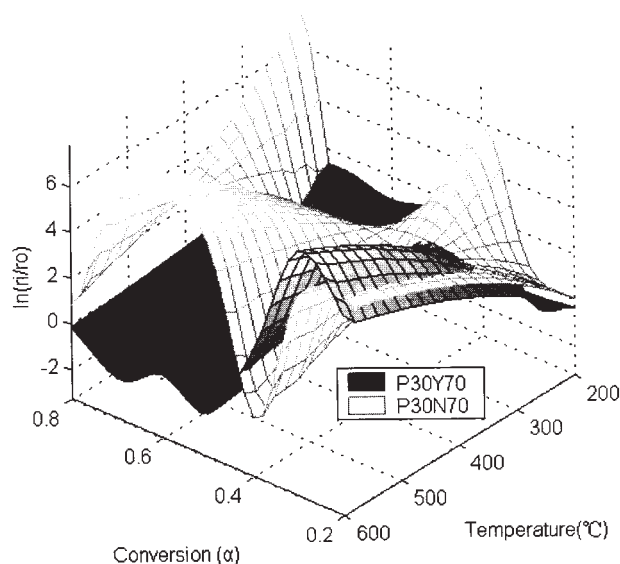


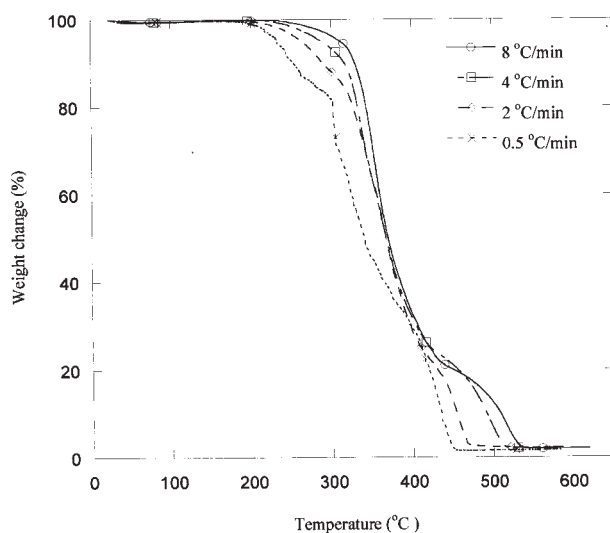
Figure 7 Rate ratio of thermal oxidative degradation of PVB with respective inorganic materials.

based on the kinetic analysis. In addition, the thermal degradation of these cases in nitrogen has the similar result of the P30Z70 case in our analysis.

DISCUSSION

The comparison of the effects of these inorganic materials on PVB thermal degradation can be evaluated by the following equations. In general, the PVB degradation rate can be defined as $r = d\alpha/dt$, where t is time, or

$$r = A \exp(-E_a/RT)f(\alpha) \quad (10)$$



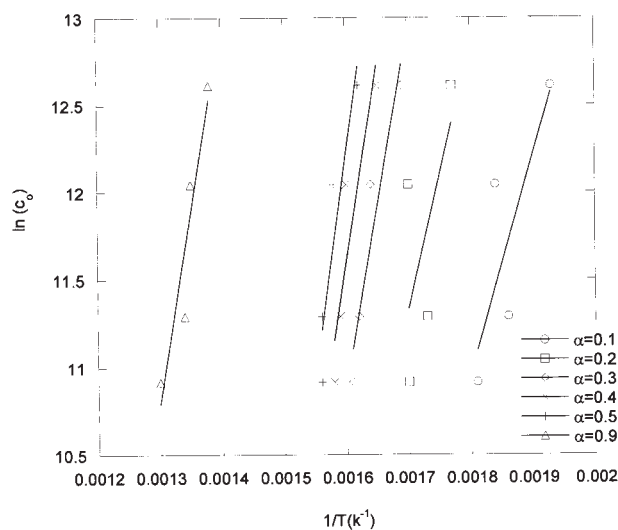
(a)

The relative ratio of the degradation rate combined with eq. (10) is expressed as

$$\ln \left[\frac{r_i}{r_o} \right] = \ln \left[\frac{A_i}{A_o} \right] - \frac{E_{ai} - E_{ao}}{RT} \quad (11)$$

where r_i is the rate of PVB with Y_2O_3 (P30Y70) or Ni (P30N70), r_o is defined as the rate of thermal degradation of the P30Z70 case in air. For instance, if the value of $\ln(r_i/r_o)$ is 0, it means that the rate of the sample (r_i) is equal to the rate of P30Z70 (r_o). The relative reaction rates can be estimated using the data in Table I. Figure 7 shows the relative reaction rates of the thermal degradation compared among P30Z70, P30Y70, and P30N70 with respect to conversion and temperature. In the initial conversion regions, both P30Y70 and P30N70 have the faster reaction rates than the P30Z70 in lower temperatures. In the higher conversion region, the P30N70 demonstrates the fastest rate among the samples, especially in higher operating temperatures. This interprets that Ni has the strongest catalytic effect on PVB thermal degradation.

The change in the E_a values associated with conversion implies that the degradation mechanism can be changed according to the isoconversional theory. In all these cases except P30N70, the E_a data are significantly changed for the conversion between 0.5 and 0.8 as shown in Table I. This implies that the mechanism of the PVB thermal degradation can be varied with respect to the chemical and physical properties of the residues left after the PVB degradation. Figure 8 shows the thermal degradation of PVB and P30Z70 in constant heating rates. The weight change curves for both cases demonstrate intersec-



(b)

Figure 8 TG curves of thermal degradation of (a) P30Z70 (b) PVB cases in constant heating rates.

tion of the lines in the region between 50 and 20% corresponding to α being 0.5 ~ 0.8. This reveals that the thermal property of the residues left behind PVB thermal degradation in that region is independent of the heating rates without the influence of the presence of the ceramics.

CONCLUSIONS

The kinetic analysis of the thermal degradation of PVB with ZrO₂, Y₂O₃, and Ni were investigated using TGA data. The reaction rates and pathways were altered by the presence of these inorganic materials except ZrO₂. The effect of ZrO₂ on the PVB degradation shows little influence; however, the catalytic effects of Y₂O₃, and Ni on PVB thermal degradation were observed strongly. The reaction rates are accelerated in lower temperatures for both PVB/Y₂O₃ and

PVB/Ni cases. Besides, the degradation period of the PVB/Ni sample demonstrated the shortest among these samples. The analytical results are useful information for the further studies of the design and operation of the burnout process.

References

1. Singhal, S. C.; Kendall, K. High Temperature Solid Oxide Fuel Cells; Elsevier Advance Technology: Oxford, UK, 2003.
2. Lewis, J. A. *Annu Rev Mater Sci* 1997, 27, 147.
3. Liao, L. C.-K.; Chiu, C.-C. *Ind Eng Chem Res* 2005, 44, 4586.
4. Lombardo, S. J.; Feng, Z. C. *J Mater Res* 2003, 18, 2717.
5. Liao, L. C.-K.; Peters, B.; Kruger, D. S.; Gordon, A.; Viswanath, D. S.; Lombardo, S. J. *J Am Ceram Soc* 2000, 83, 2645.
6. Liao, L. C.-K.; Liao, J.-Y.; Chen, Y.-T. *J Appl Polym Sci* 2004, 93, 2142.
7. Liao, L. C.-K.; Liao, J.-Y. *Ind Eng Chem Res* 2004, 43, 1938.
8. Liao, L. C.-K.; Hsieh, Y. H. *Polym Degrad Stab* 2005, 89, 545.