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Thermochimica Acta 378 (2001) 87–96

thermochimica acta

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Preparation of NiO through $NaNO_3$–KNO_3 eutectic melt and its catalytic activity during the decomposition of polystyrene

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Received 24 November 2000; received in revised form 26 April 2001; accepted 20 May 2001

Abstract

The decomposition of basic nickel carbonate in the presence and absence of $NaNO_3$ (sodium nitrate)–KNO_3 (potassium nitrate) eutectic melt has been studied by employing isothermal TG and dynamic TG–DSC techniques. The rate constants for the decomposition in the presence of eutectic melt were found to be higher than when carbonate alone was heated. In both cases, nickel oxide was found to be the end product. Catalytic activities of nickel oxide obtained by the two methods were tested for their efficiency in decomposition of polystyrene (PS). It was found that at higher temperature (330 and 360°C), the nickel oxide obtained from eutectic melt was more active than that obtained by direct decomposition. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: TG–DSC; Decomposition; Kinetics; Nitrates; Polystyrene

1. Introduction

Molten nitrates are frequently used as nonaqueous solvents for studying a number of chemical reactions [1]. Nitrate eutectics have considerably lower melting temperatures compared to the individual components and hence easier to handle. Recently, decomposition reactions of a number of metal salts using nitrate eutectic melts have been studied [2–6], and it has been found that the decomposition reactions occur at a much lower temperature. Since in most of the cases, the metal oxides were obtained as the end product, it is to be expected that their surface area will be high and they may act as better catalysts.

In the present paper, the decomposition of basic nickel carbonate in the presence and absence of $NaNO_3$ (sodium nitrate)–KNO_3 (potassium nitrate) eutectic has been studied by using TG–DSC studies. The reaction product formed was analyzed by chemical method and powder X-ray diffraction technique. The thermal decomposition of polystyrene (PS) was also studied in the presence of NiO.

2. Experimental

2.1. Materials

$NaNO_3$, KNO_3, and $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$ all from Qualigens were used.

2.1.1. Polystyrene

Polystyrene was prepared from styrene monomer received from Synthetic and Chemical Ltd., Bareilly, India. Styrene was first purified by distillation under reduced pressure at 50 ± 1°C and polymerized by adding benzoyl peroxide ($10\ g\ l^{-1}$) and placing the mixture in a test tube in thermostat for 48 h at

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PII: S0040-6031(01)00577-9

50 ± 1°C. The viscous polymer was cured at 50°C for 15 days to get a hard mass in the form of a cylinder [7].

2.1.2. *$NaNO_3$–KNO_3 eutectic*

Dried samples of sodium nitrate and potassium nitrate were mixed in 45:55 ratio (wt.%) in a clean test tube. The mouth of the test tube containing the nitrate mixture was sealed and kept in a furnace at a temperature slightly higher than the melting points of the components. When the entire mass melted, the molten liquid was quenched suddenly to room temperature. The process of heating and cooling was repeated several times and ultimately the solidified material was removed from the test tube and crushed into fine powder. This was carried out to produce a homogeneous mixture of the two components. The melting point of the eutectic mixture was found to be 226°C.

2.2. *Methods*

2.2.1. *Isothermal TG studies*

Isothermal TG experiment on nickel carbonate alone in presence of $NaNO_3$–KNO_3 eutectic mixture, and polystyrene with 2% NiO were performed with a manual thermogravimetric analyzer under ambient conditions in an atmosphere of air. Gold crucible was used in the experiment and hung in an electric furnace with gold wire. The temperature was recorded with a temperature indicator PI (LC-40). The sample was maintained at constant temperature with the help of a dimerstat. The mass loss was noted as a function of time. Each experiment was repeated three times at different temperatures.

2.2.2. *TG–DSC studies*

Simultaneous TG–DSC studies on basic nickel carbonate, nickel carbonate in $NaNO_3$–KNO_3 eutectic, polystyrene, nickel carbonate with polystyrene and nickel carbonate in $NaNO_3$–KNO_3 eutectic with polystyrene were performed with Setaram TG–DSC 92-16 apparatus at BARC, Mumbai, under argon atmosphere at a heating rate of 10°C min^{-1} under argon atmosphere.

2.2.3. *Gravimetric estimation*

Solid reaction products obtained from thermogravimetric studies were washed with water to separate insoluble oxide. Nickel was estimated gravimetrically as the oxide by a standard method [8].

2.2.4. *Analysis of the gaseous product*

The evolved gas was tested in the usual way and found to be CO_2 and water vapor. CO_2 was tested by passing through lime water where as water vapor was tested by anhydrous copper sulfate.

2.2.5. *Powder X-ray diffraction studies*

The powder X-ray diffraction patterns of the residues after TG were recorded with an X-ray diffractograph (XRD-5 General Electric, USA) using Cu Kα radiation.

3. Results and discussion

TG and DSC curves of basic nickel carbonate are shown in Fig. 1. The TG response of the compound exhibited two mass loss steps. The first step appeared to consist of two consecutive reactions which involved loss of water of crystallization and dehydration (50–250°C). The two steps overlapped and were not clearly resolved. The second step of mass loss started at 250°C and was completed at 360°C. The final mass loss corresponded to the formation of NiO which was confirmed by powder X-ray diffraction data and chemical analysis ($\text{NiO}_{\text{Exp}} = 15.70\%$, $\text{NiO}_{\text{Cal}} = 15.80\%$).

DSC curve shows three broad endotherms at about 50, 130, and 320°C. The first small peak was due to the removal of adsorbed water molecules and the second endotherm to the removal of water of crystallization and dehydration. A broad endotherm at 320°C indicated the decomposition of carbonate.

$$\begin{aligned} &NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O \\ &\quad \rightarrow NiCO_3 \cdot 2Ni(OH)_2 + 4H_2O, \\ &NiCO_3 \cdot 2Ni(OH)_2 \rightarrow 3NiO + 2H_2O + CO_2. \end{aligned}$$

The kinetics of thermal decomposition was studied by isothermal TG between 220 and 340°C. In a solid-state reaction leading to the evolution of the gaseous product, the fraction decomposed α can be calculated from Eq. (1) as follows:

$$\alpha = \frac{w_0 - w_t}{w_0 - w_\text{f}}, \tag{1}$$

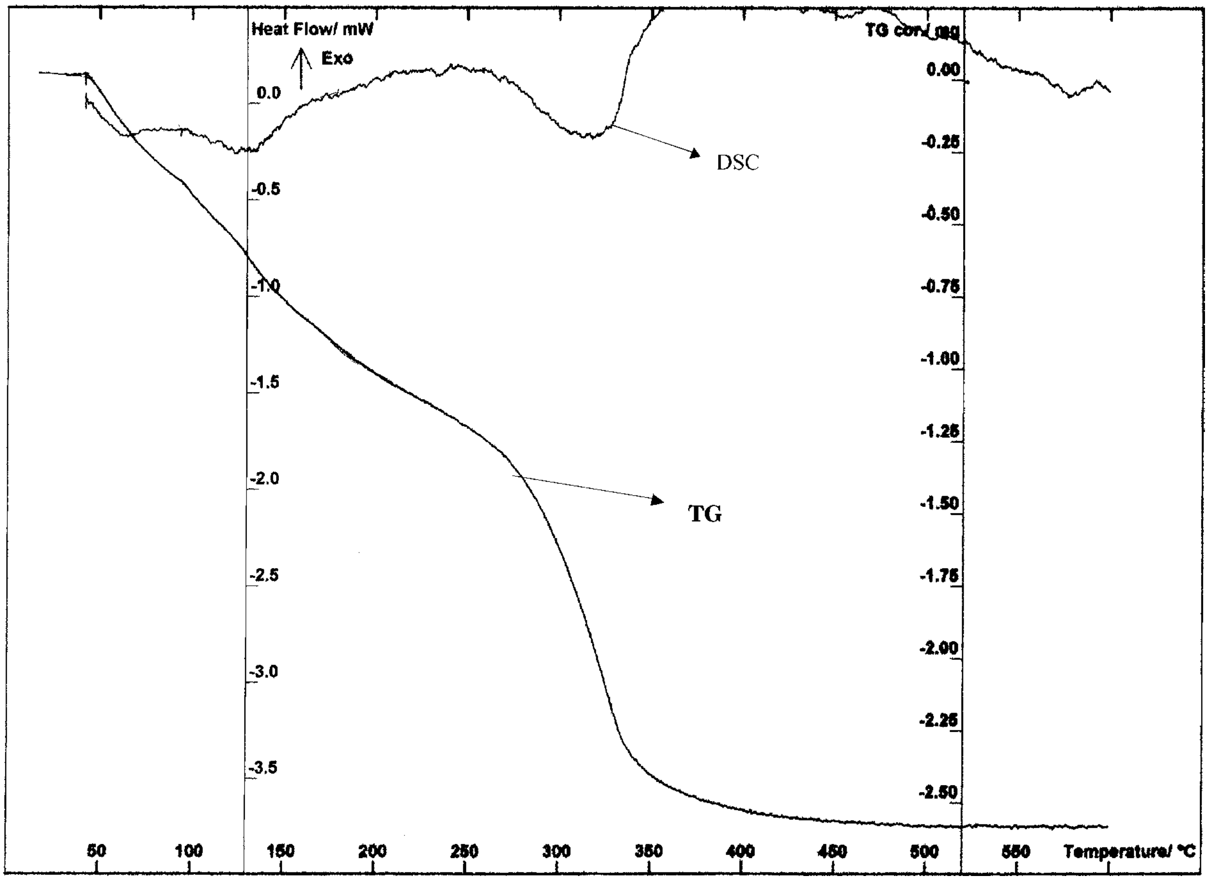

Fig. 1. TG and DSC curves for the decomposition of $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$.

where w_0, w_t, and w_f are initial, actual at any time t, and final sample weights, respectively. The values of α are given in Table 1. The kinetic data obeyed Eq. (2):

$$1-(1-\alpha)^{1/2}=k_1t, \tag{2}$$

where k_1 is a rate constant. When $1-(1-\alpha)^{1/2}$ is plotted against t, straight line showing the validity of Eq. (2) is obtained (Fig. 2). the rate constants k_1 are given in Table 2, the activation energy for this reaction calculated from Arrhenius plot is also given in the same table.

TG and DSC curves of the decomposition of basic nickel carbonate in eutectic melt are shown in Fig. 3. The TG had four mass loss steps (50–130, 200–275, 300–400, and 500–600°C). DSC curve showed number of endothermic peaks, details of which are given in Table 3. It is possible that there is a double-decomposition reaction between nickel carbonate and nitrate eutectic forming nickel nitrate, which decomposes to nickel oxide [9]. This can be inferred from broad and complicated peaks between 300 and 400°C. Presence of NiO and unreacted $NaNO_3$ and KNO_3 has been confirmed by X-ray diffraction.

When basic nickel carbonate was heated with molten $NaNO_3$–KNO_3 eutectic, decomposition started with a much faster rate and at a lower temperature as compared to that without eutectic. The fraction decomposed α were calculated and the values are given in Table 1. Kinetics of the reaction were studied by isothermal TG and the data obeyed Jander's Eq. (3):

$$[1-(1-\alpha)^{1/3}]^2=k_2t, \tag{3}$$

Table 1
The value of fraction decomposed at different time intervals at different temperatures in different systems

System	Temperature (°C)	Fraction decomposed at different time intervals (α)																	
		5 min	10 min	15 min	20 min	25 min	30 min	35 min	40 min	45 min	50 min	55 min	60 min	65 min	70 min	75 min	80 min	85 min	90 min
$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$	220	0.54	0.588	0.614	0.652	0.695	0.727	0.77	802	0.839	0.882	0.914	0.962	1					
	260	0.593	0.627	0.675	0.696	0.757	0.787	0.844	883	0.913	0.965	1							
	300	0.636	0.681	0.723	0.761	0.822	0.871	0.913	950	1									
	340	0.699	0.761	0.818	0.876	0.925	1												
$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ in $NaNO_3$–KNO_3 eutectic	220	0.642	0.729	0.793	0.842	0.902	0.932	0.958	1										
	260	0.724	0.814	0.884	0.925	0.959	0.981	1											
	300	0.767	0.865	0.927	0.963	0.985	1												
	340	0.790	0.924	0.978	1														
Polystyrene + 2% NiO	270	0.11	0.21	0.26	0.34	0.39	0.45	0.5	55	0.60	0.64	0.70	0.72	0.77	0.80	0.83	0.87	0.89	
	300	0.18	0.28	0.39	0.45	0.51	0.58	0.64	72	0.75	0.8	0.84	0.89	0.94	1				
	330	0.16	0.31	0.4	0.5	0.59	0.69	0.76	83	0.89	0.97	1							
	360	0.21	0.43	0.64	0.81	0.94	1												
Polystyrene + 2% NiO (obtained from eutectic)	270	0.089	0.19	0.238	0.24	0.29	0.32	0.37	41	0.46	0.48	0.54	0.58	0.62	0.68	0.71	0.72	0.76	
	300	0.06	0.45	0.22	0.29	0.38	0.44	0.48	0.54	0.6	0.64	0.7	0.76	0.8	0.84	0.88	0.95	0.96	1
	330	0.19	0.32	0.44	0.56	0.66	0.78	0.84	0.92	0.97	1								
	360	0.33	0.59	0.82	0.94	1													

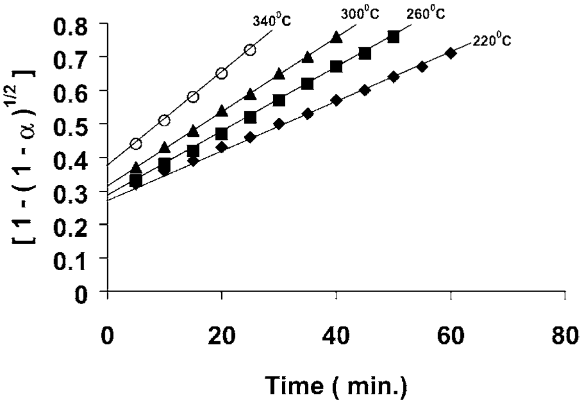

Fig. 2. Verification of kinetic Eq. (2) for the decomposition of $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$.

Table 2
Kinetic parameters of Eq. (2) for the decomposition of $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$

Temperature (°C)	$k_1 \times 10^3$ (min^{-1})	E (kJ mol^{-1})
220	6.9	
260	9.6	14.8
300	11.1	
340	14.0	

where k_2 is the rate constant. When $[1-(1-\alpha)^{1/3}]^2$ is plotted against t, straight lines showing the validity of Eq. (3) are obtained (Fig. 4). The rate constants k_2 are given in Table 4, the activation energy for this reaction calculated from the Arrhenius plot is also given in the table.

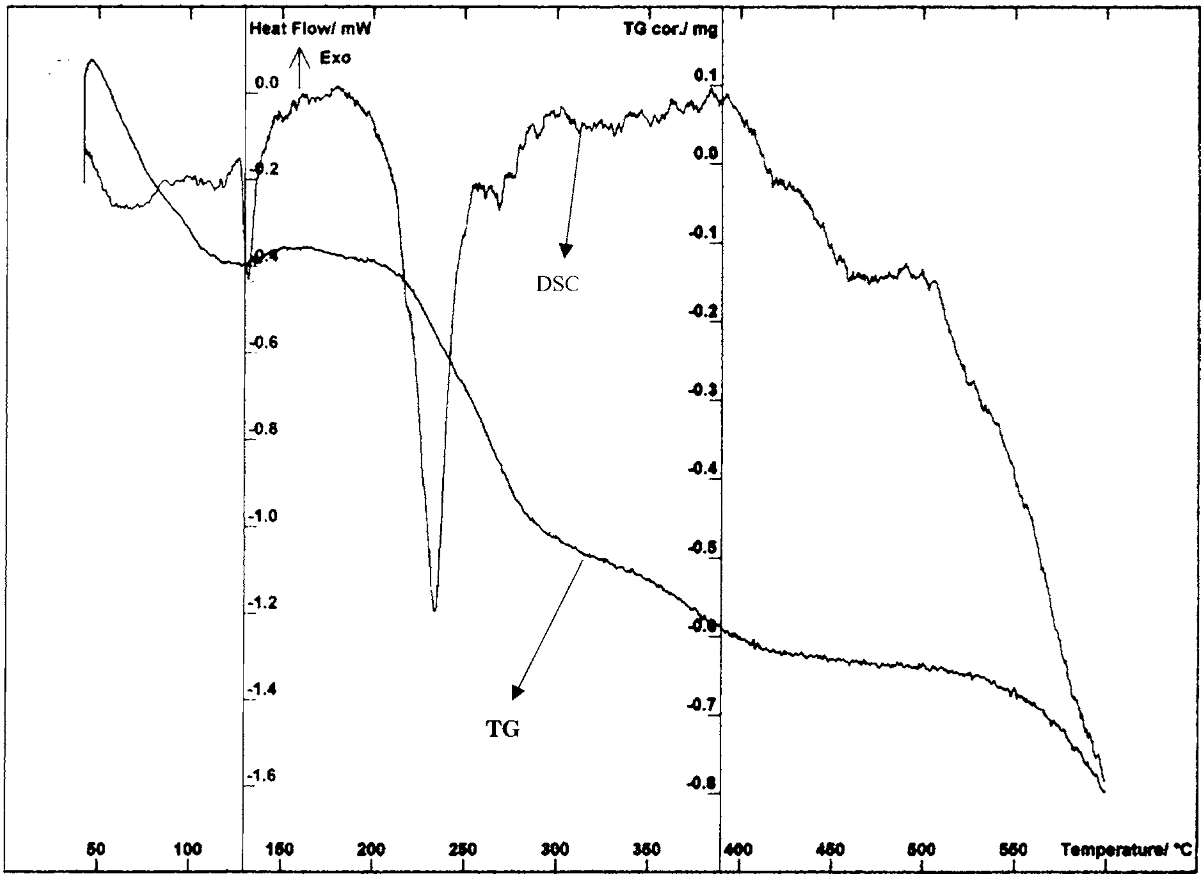

Fig. 3. TG and DSC curves for the decomposition of $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$ in $NaNO_3$–KNO_3 eutectic melt.

Table 3
DSC peaks (endothermic) and their interpretation for the decomposition of $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ in $NaNO_3$–KNO_3 eutectic

DSC peak temperature (°C)	Process
50	Removal of adsorbed water
120	Dehydration
130	Phase transformation of KNO_3
225	Melting of eutectic
260–400	Double-decomposition reaction leading to the formation of NiO
≈500	Slow sublimation of nitrate eutectic and its decomposition

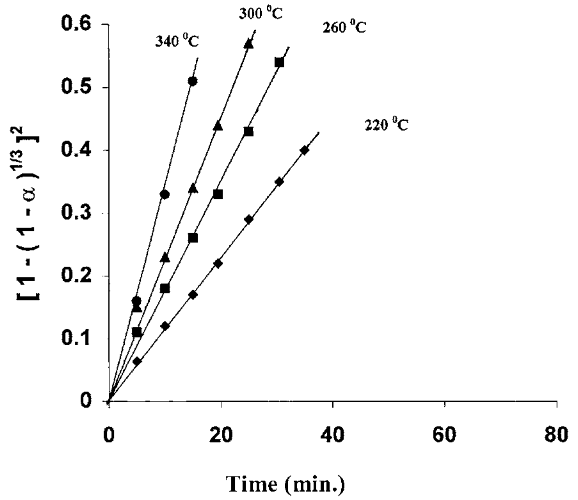

Fig. 4. Verification of kinetic Eq. (3) for the decomposition of $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ in $NaNO_3$–KNO_3 eutectic melt.

The fraction decomposed at any time t at any given temperature in the presence of eutectic melt is much higher than in its absence. The rate constant in presence of eutectic melt is also much higher. The results show that basic nickel carbonate decomposes at a much faster rate in the presence of molten nitrate eutectic.

Table 4
Kinetic parameters of Eq. (3) for the thermal decomposition of $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ in $NaNO_3$–KNO_3 eutectic

Temperature (°C)	$k_2 \times 10^2$ (min^{-1})	E ($kJ\ mol^{-1}$)
220	1.2	
260	1.9	23.1
300	2.3	
340	3.4	

TG–DSC curves for the decomposition of polystyrene are shown in Fig. 5. TG indicated that there was a one-step mass loss from 250 to 400°C and the total mass was lost at about 400°C. This indicates that total PS is decomposed into vapor. It has already been reported that polystyrene degrades at elevated temperature to a mixture of low molecular weight compounds about half of which is styrene [10,11]. DSC curve shows sharp endotherms at 350, 380, and 385°C and one sharp exotherm peak at 400°C and a broad exotherm between 450 and 550°C. These peaks indicate that polystyrene does not degrade in one step and there are a number of degradation products which are formed at different temperatures. The process may be overlapping and that is why not detected by TG technique.

Thermal decomposition of PS in presence of basic nickel carbonate was studied by using TG–DSC technique (Fig. 6). The TG mass loss up to 150°C was due to dehydration of basic nickel carbonate. Further mass loss occurs between 250 and 475°C and the curve consists of different overlapping processes. In this temperature range, decarboxylation of nickel carbonate and degradation of PS take place. DSC curve shows number of endotherms corresponding to TG curve. The mass remaining at the end correspond to NiO indicating that during the process, $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ is converted to NiO and PS degradates.

The isothermal decomposition of PS in presence of 2% NiO obtained from the thermal decomposition of basic nickel carbonate has been studied and the kinetic data is found to obey Eq. (4):

$$[-\ln(1-\alpha)]^{1/2} = k_3 t. \tag{4}$$

When $[-\ln(1-\alpha)]^{1/2}$ is plotted against t, straight lines are obtained (Fig. 7). The rate constants calculated are

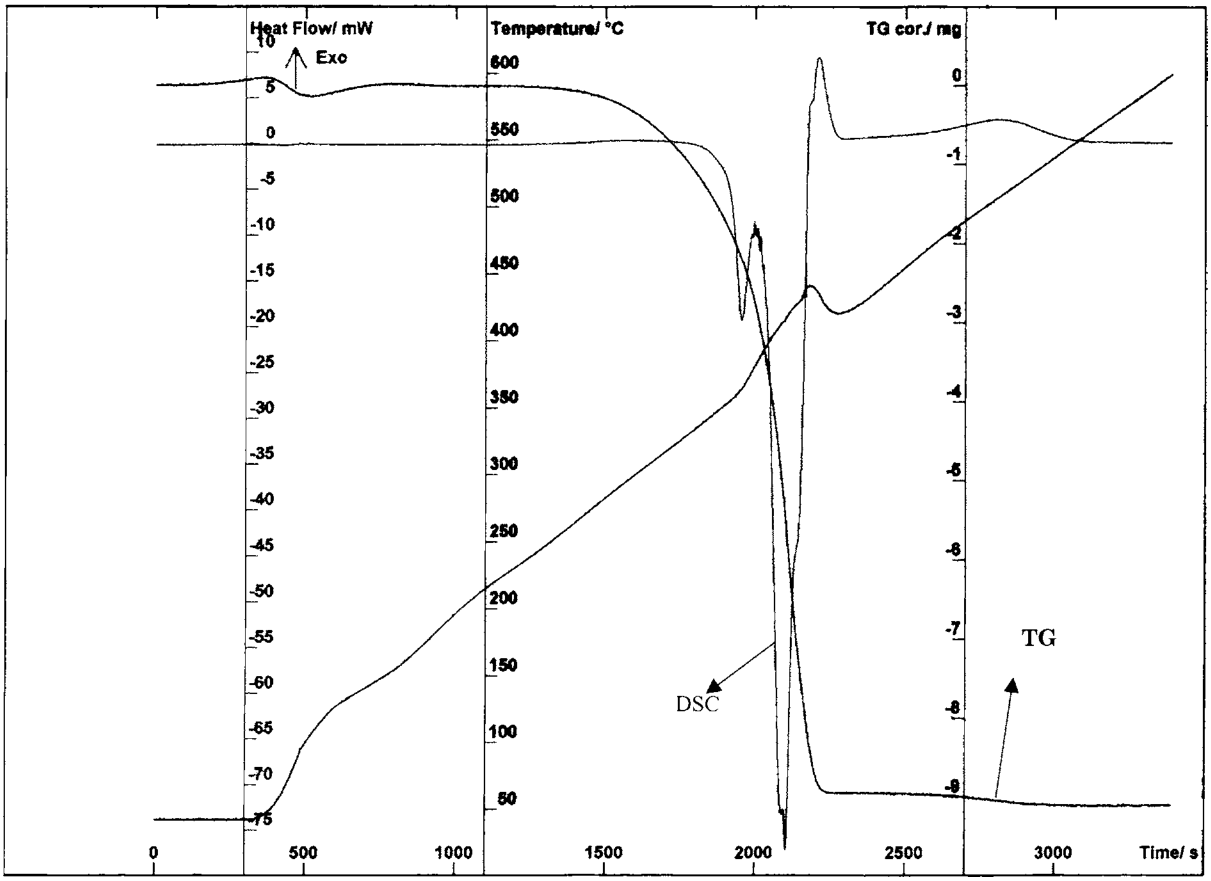

Fig. 5. TG and DSC curves of polystyrene.

given in Table 5. From the Arrhenius plot, the activation energy was calculated and found to be 56.3 kJ mol^{-1}.

When basic nickel carbonate mixed with $NaNO_3$–KNO_3 eutectic is heated with PS, the TG–DSC curves are shown in Fig. 8. In TG curve, a mass loss below 120°C is due to dehydration of basic nickel carbonate. Further, a mass loss starting from 200°C and completing at about 450°C followed by different mass loss steps are obtained. These may be due to decomposition of basic nickel carbonate in nitrate eutectic melt and the thermal decomposition of PS in presence of freshly formed NiO. DSC curve shows number of endothermic peaks. A broad peak at around 50°C may be due to dehydration and a sharp peak at around 120°C is due to phase transformation of KNO_3. A peak at around 230°C with a shoulder at around 225°C is due to fusion of eutectic mixture followed by decarboxylation of nickel carbonate. Endothermic peaks at 300 and 400°C may be due to thermal degradation of PS. After that there are broad exothermic peaks which may be due to decomposition of eutectic mixture followed by continuous vaporization.

Table 5
Kinetic parameters of Eq. (4) for the thermal decomposition of polystyrene with 2% NiO

Temperature (°C)	$k_3 \times 10^3$ (min^{-1})	E (kJ mol^{-1})
270	13.5	
300	16.8	56.3
330	24.4	
360	54.0	

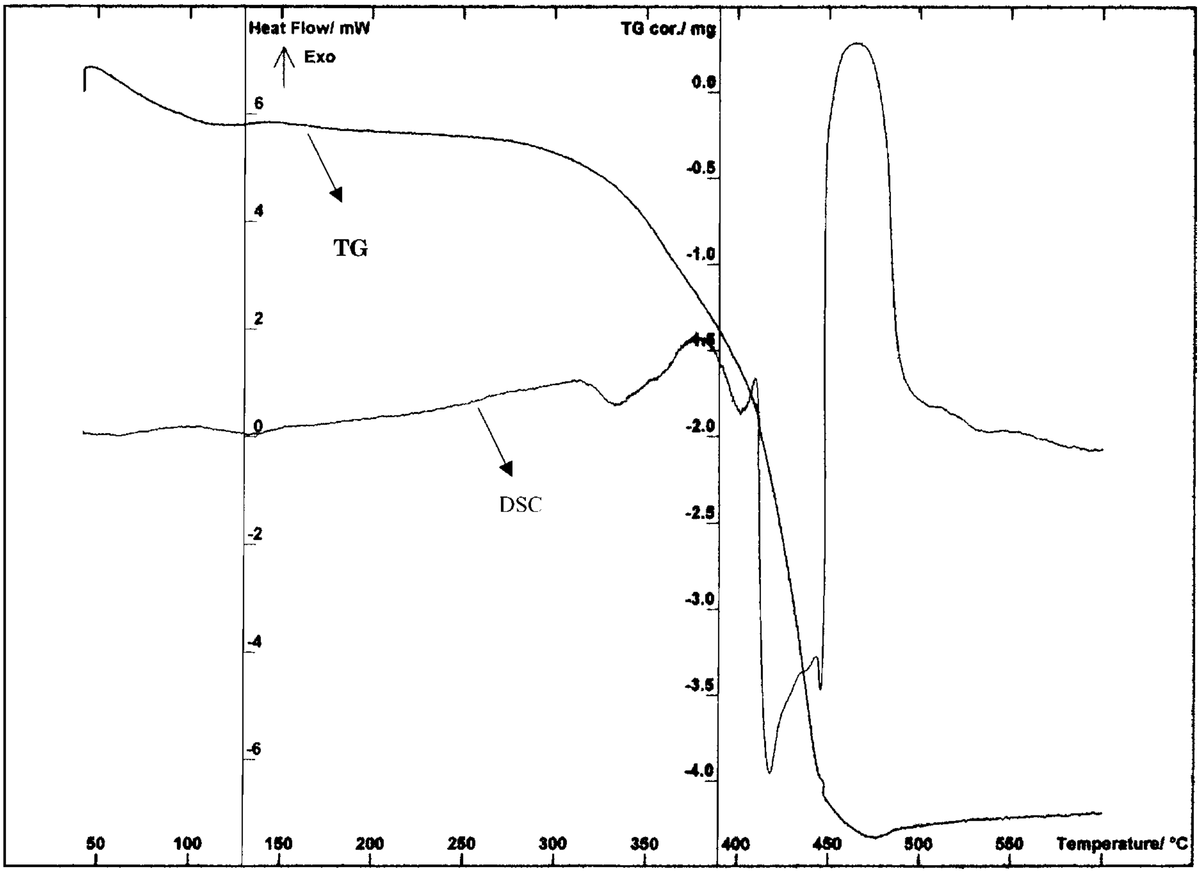

Fig. 6. TG and DSC curves for a mixture of $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$ (50%) + polystyrene (50%).

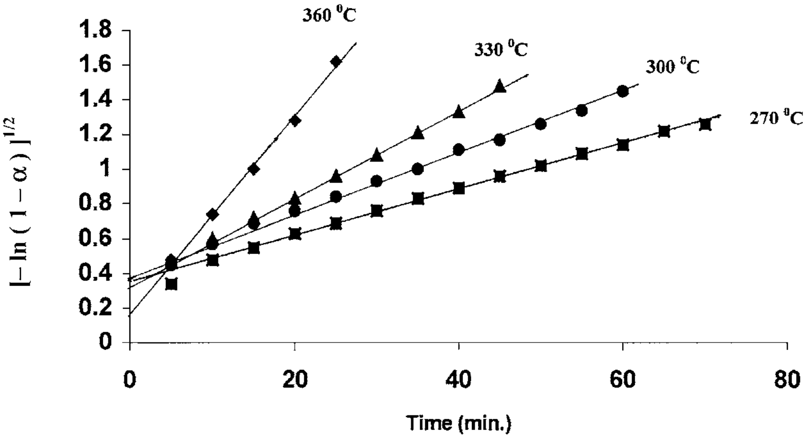

Fig. 7. Verification of kinetic Eq. (4) for the decomposition of polystyrene in presence of 2.0 wt.% NiO.

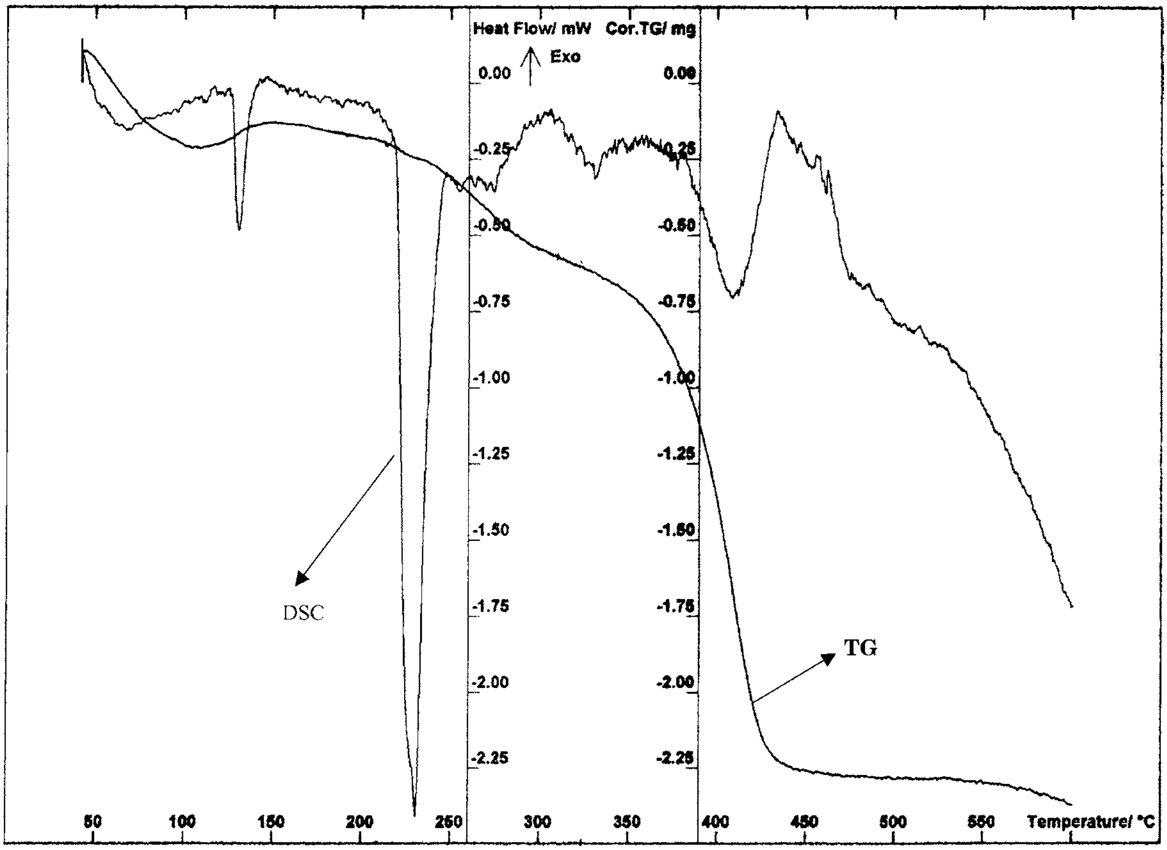

Fig. 8. TG and DSC curves for a mixture of $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$ (12.5%) + polystyrene (12.5%) + $NaNO_3$–KNO_3 (75%).

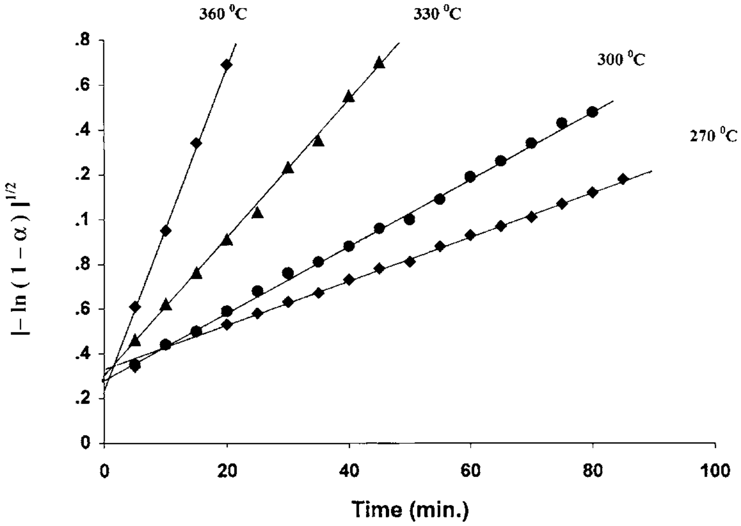

Fig. 9. Verification of kinetic Eq. (4) for the decomposition of polystyrene in presence of 2% NiO (obtained from eutectic).

Table 6
Kinetic parameters of Eq. (4) for the thermal decomposition of polystyrene with 2% NiO (obtained from eutectic)

Temperature (°C)	$k_3 \times 10^3$ (min^{-1})	E (kJ mol^{-1})
270	9.6	
300	14.8	51.4
330	30.8	
360	74.0	

Isothermal kinetics of degradation of PS in presence of 2% NiO obtained from nitrate eutectic melt was studied and the kinetic data obeyed Eq. (4) (Fig. 9). The rate constants were calculated and are given in Table 6. The energy of activation was calculated from Arrhenius plot and found to be 51.4 kJ mol^{-1}. The results show that at higher temperature, NiO obtained from eutectic melt decomposes polystyrene at a faster rate with lower energy of activation. This may be due to higher surface area of NiO obtained from eutectic melt.

4. Conclusions

The overall results show that basic nickel carbonate decomposed faster in presence of $NaNO_3$–KNO_3 melt and the end product in both the cases were NiO. NiO obtained from eutectic melt acted as a better catalyst for the thermal decomposition of polystyrene at 330 and 360°C.

Acknowledgements

One of us (AKO) is thankful to the CSIR, New Delhi, for financial support. The authors are thankful to the BARC, Mumbai, for providing necessary facilities for X-ray diffraction and simultaneous TG–DSC studies.

References

[1] E. Huheey, E.A. Keiter, R.L. Keiter, Textbook of Inorganic Chemistry, Principles of Structure and Reactivity, 4th Edition, Harper Collins, New York, 1993, pp. 359–373.
[2] D.H. Kerridge, A. Zellipour, Thermochim. Acta 159 (1990) 163–170.
[3] D.H. Kerridge, A. Zellipour, Thermochim. Acta 162 (1990) 311–323.
[4] D.H. Kerridge, W.M. Shakir, Thermochim. Acta 178 (1991) 295–303.
[5] D.H. Kerridge, W.M. Shakir, Thermochim. Acta 182 (1991) 107–122.
[6] H.M.A. Abood, D.H. Kerridge, Thermochim. Acta 198 (1992) 297–302.
[7] K. Kishore, V.R. Paiverneker, M.N.R. Nair, J. Appl. Polym. Sci. 20 (1976) 2355–2365.
[8] A.I. Vogel, A Textbook of Quantitative Inorganic Chemistry, Longman, New York, 1961.
[9] R.P. Rastogi, N.B. Singh, S.P. Pandey, Indian J. Chem. 21A (1982) 456–459.
[10] F.W. Billmeyer Jr., A Textbook of Polymer Science, 2nd Edition, Wiley, New York, 1962, p. 405.
[11] H.R. Allock, F.W. Lampe, Contemporary Polymer Chemistry, Prentice-Hall, Englewood Cliffs, NJ, 1981, p. 209.