KINETIC STUDY ON PYROLYSIS OF PVC BY NiO NANOPARTICLES

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ABSTRACT

In this work, the catalytic effect of nano-NiO particles on the pyrolysis of PVC has been investigated by thermogravimetry technique. For this study, the catalytic decomposition of PVC over several nano-NiO samples with different particle size and morphology has been investigated. The kinetic analysis has been carried out using different kinetic models. The catalyst has a remarkable influence on the initial decomposition process. It shifted the initial decomposition temperature of the PVC to lower temperatures with decreasing the NiO – particle size. Evaluation of the catalytic activity of nano-NiO particles on pyrolyzing PVC was carried out in comparison with that of micro-NiO in the same condition.

INTRODUCTION

Accumulation of enormous amounts of plastic waste produced all over the world has negative implications on the environment. The pyrolysis of organic materials has received renewed attention due to the possibility of converting these wastes into useful valuable chemicals [Pinto *et al.*, (1999)]. The addition of a catalyst could not only improve the quality of products obtained from pyrolysis of plastic wastes and lower the temperature of decomposition, but could also enable a given selectivity to a certain product to be achieved [Pinto *et al.*, (1999)].

As well known, nanomaterials possess unique properties in various fields on account of different effects in terms of volume, quantum size, surface and macroscopic quantum tunnel [Li *et al.*, (2008)]. Therefore,

nanomaterials have been employed as catalysts to improve the thermal decomposition characteristics of solid materials [Shi *et al.*, (2008)]. In recent years, nickel oxide (NiO) nanoparticles have received lots of attention for the electronic, magnetic and especially catalytic properties [Wei *et al.*, (2003)].

Thermogravimetry (TG) is one of the techniques used to analyze the primary reactions of the thermal decomposition of solids, which has been widely used to study the thermal decomposition of polymers and other materials [Bockhorn *et al.*, (1996)] and [Wei *et al.*, (2009)]. The interpretation of the experimental data can provide information on number of different processes that take place in the reaction and their corresponding kinetic constants, if adequate kinetic models and correlation procedures are applied [Bockhorn *et al.*, (1999)] and [Marcilla *et al.*, (2002)].

Kinetic modeling is a powerful and sound technique of data reduction. The advantages of this practice are obvious for engineering purposes. The kinetic parameters obtained allow the fast computer reproduction of the data as well as the interpolation, especially in the case of complex reactions. Obviously, to develop a really mechanistic kinetic model, or being more ambitious, the actual kinetic model is almost an impossible task, since a large number of interacting processes (both physical and chemical process) are always involved in solid reactions [Marcilla *et al.*, (2002)].

The objective of this work is to study the thermal pyrolysis of PVC with nano-NiO. The weight loss of the sample as a function of temperature has been determined by TG, at only one heating rate and different particle sizes of NiO. Different kinetic models have been applied to the TG data obtained.

EXPERIMENTAL

NiO nanopowders were prepared by methods described elsewhere. Sample (N₁) was prepared by precipitation of nickel sulfate using urea solution at 95°C followed by drying at 75°C and then calcination at 350°C. Samples (N₂, N₃) were prepared by sol-gel technique using citric acid at 80°C, followed by drying at 110°C and then calcined at 400 and 600°C, respectively. The main characteristics of the

prepared catalysts and the notation used in this work are listed in **Table (1).** Micro-NiO powder (N_4) (325 mesh, approximately 44μm, purchased from Alfa Aesar) was used as a reference catalyst. The PVC powder was purchased from Sigma-Aldrich Chemie GmbH, with an average particle size of ~50μm.

Thermogravimetric runs were performed using a Schimadzu TGA-50H thermal analyzer. Sample masses lying between 4 and 25 mg were used at a heating rate of 10°C/min. All samples were in the powder form and the study was carried out using initial mixtures (catalyst/PVC= 3% by weight). The samples were placed in open platinum pans. The carrier gas was N_2 (99.99% minimum purity), at a flow rate of around 20 ml STP min^{-1}.

Kinetic analysis:

Historically model-fitting methods were widely used because of their ability to determine the kinetic parameters directly. On the other hand, is a conversional method, does not compute a frequency factor nor determine reaction models which are needed for a complete and accurate kinetic analysis. In solid state kinetics, mechanistic interpretations usually involve identifying a reasonable reaction model [**John et al., (2012)**] because information about individual reaction steps is often difficult to obtain. A model can describe a particular reaction type and translate it mathematically into a rate equation. Many models have been proposed in solid-state kinetics and these models have been developed based on certain mechanistic assumptions. Solid-state kinetic reactions can be mechanistically classified as nucleation, geometrical contraction, diffusion and reaction order models [**Galwey et al., (1999)**]. The TG data were subjected to weighted least squares analysis by all kinetic models given in [**Galwey et al., (1999)**].

Theoretical back ground:
Multiple kinetic models were used to fit the thermogravimetric data; they include the conversional analysis method, the *n*th-order Arrhenius model, and the extended-Prout–Tompkins model. Briefly, in all three methods the rate equation for fraction reacted begins with:

$$d\alpha /dt = k \, f\,(\alpha) = A \, \exp^{-Ea/RT(\alpha)} \tag{1}$$

where t is the time, k is the Arrhenius rate constant, A is the pre-exponential factor, E_a is the apparent activation energy, R is the gas constant, T is the absolute temperature, and $f(a)$ is the reaction model, the conversion fraction (a) at any temperature is $a = (m_0 - m_T)/(m_0 - m_f)$ where m_0, m_T and m_f represents the initial, actual and final mass of the investigated sample, respectively.

In the Friedman as a conversional method, Eq. (1) is rearranged to the following: [**Friedman et al., (1963)**].

$$\ln (da/dt_a) = -E_a/RT_a + \ln [A_a f(a)] \tag{2}$$

By plotting ln (da/dt_a) vs. $1/T_a$ (i.e. the temperature at each fraction point, a), and fitting the data to a straight line, the values for E_a and $\ln\{A_a f(a)\}$ can be calculated. These values are dependent on the extent of the reaction. Typically the first and last 10% of the reaction are erroneous due to small signal-to-noise ratios of the data.

The Coats-Redfern method [**Coats et al., (1964)**] has been widely used for calculating kinetics in solid reactions because it is simple and easy to use. The calculation based on the following equations:

$$\ln [G(a)] = -E/RT + \ln(AR/\beta E) \tag{3}$$

Where

$$G(a) = -\ln (1-a)/T^2 \qquad \text{(for n=1)} \tag{4}$$

$$G(a) = -(1-(1-a)^{1-n})/(1-n)T^2 \qquad \text{(for } n \neq 1\text{)} \tag{5}$$

If the reaction order is correct, the plot of ln [G (a)] versus $1/T$ should be a straight line. The activation energy E can be obtained from the slope, and the pre-exponential factor A can be obtained from the intercept.

In the n th order Arrhenius analysis $f(a)$ [**Elbeyli, et al., (2004)**]. is replaced with the term $(1-a)^n$ resulting in Eq. (3):

$$dq/dt = k f(a) = Ae^{-E/RT} (1-a)^n \tag{6}$$

Where n is unit less variable associated with the reaction order.

RESULTS AND DISCUSSION

Catalytic study:

Figure 1 shows the TG curves of PVC pyrolysis with addition of nano-NiO and micro-NiO, respectively (the quantities of the catalyst were already subtracted in the TG curves), or without any catalyst. The TG of all samples showed that the pyrolysis occurred in well defined three stages. The thermal behavior of PVC pyrolysis without any catalyst is similar to that reported in the literature [Garcı-Quesada *et al.*, (2001)]. When comparing the TG curves of PVC with and without a catalyst, it can be seen that both of nano- and micro-NiO particles had a positive effect on the pyrolysis of PVC, and the effect of nano-NiO was superior to that of micro-NiO particles. The catalyst altered the decomposition of PVC to occur at a lower temperature. The thermal comparisons of PVC pyrolysis with and without present of catalyst are listed in table (2). Table (2) shows that the initial and final temperatures of decomposition of PVC in the presence of catalyst are lower than that of pure PVC. The acceleration pyrolysis process according the TG curves follows the sequence:
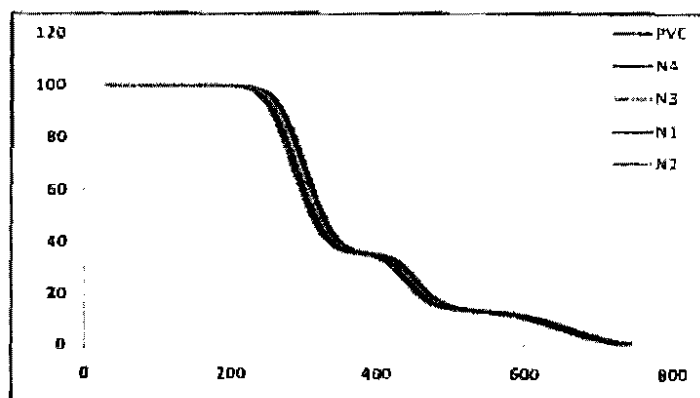
$$PVC/N_2 > PVC/N_1 > PVC/N_3 > PVC/N_4 > PVC$$

Fig. (1): Pyrolysis of PVC in absence and presence of NiO catalyst.

Kinetic calculations:

In the present study, kinetic analysis of thermal analysis data for the first step in the pyrolysis of PVC is performed using three computational methods: Friedman, Arrhenius and Coats-Redfern. Based on Friedman method the activation energy (E_a) without having to presuppose a certain mode have been determined by using Eq. (2) at different α values. The calculated activation energy (E_a) values of the decomposition reaction of PVC are given in Table (3). It can be seen a variable (E_a) with conversion fraction α that is an indication of a complex reaction, which will be more serious if the total reaction involves the competitive reactions. Applying the average value of (E_a) within □ of 0.20–0.80 rather than the entire range was strongly recommended because most reactions, especially solid-state ones, are not stable at the beginning and ending periods. Different from solution reaction, solid-state reaction usually contains a diffusion process, the well-known mass and heat-transfer phenomenon [Dileka et al., (2011)] at the beginning period. It generates temperature and partial pressure gradient. Consequently, it generates reaction gradient from the outer to the inner surface of the solid sample.

Assuming that the pyrolysis in this work is being controlled primarily by chemical decomposition, the Coats -Redfern method has been also applied to calculate the kinetic parameters of PVC pyrolysis, with and without catalyst. In the Coats-Redfern method, reaction orders were assumed to have the values from 0 to 2.5 in α range of 0.2 to 0.8. R^2 values (best- fit criteria) for all the orders were calculated and plotted against the n values as shown in Fig. 2. R^2-n curves have maximum n values corresponding to the more appropriate kinetic mechanism, from which optimal values of pyrolysis reaction order were calculated. These optimal values of n = 1.25 were put in Eq. (6) (the nth order Arrhenius method) to calculate the E_a and A values by plotting the left side of Eq. (6) vs. 1/T. The slope of the line is used to calculate E_a and A is determined from the intercept of line. The average n, E_a and A of pyrolysis reactions were listed in Table (3).

Table (1): Main characteristic of PVC and NiO catalyst.

Material	Preparation Method	Particle siz of NiO (nm)	Surface Morphology
N_1	Precipitation in presence of urea	3 nm	Nano spherical
N_2	Sol-gel method, and calcination at 400° C	32 nm	Mixed shapes and mixed phases of NiO and impurities of Ni
N_3	Sol-gel method, and calcination at 600° C	41 nm	Nanoplates
N_4	(AlfaAesar)	44 µm	
PVC	(Sigma Aldrich)	50 nm	Fibrous powder

Table (2): Kinetic parameters for pyrolysis of PVC and NiO/PVC using Friedman analysis.

α	PVC		PVC/N₄		PVC/N₃		PVC/N₂		PVC/N₁	
	E ($kJ\,mol^{-1}$)	A (min^{-1})	E ($kJ\,mol^{-1}$)	A (min^{-1})	E ($kJ\,mol^{-1}$)	A (min^{-1})	E ($kJ\,mol^{-1}$)	A (min^{-1})	E ($kJ\,mol^{-1}$)	A (min^{-1})
0.02	165	2.2×10^{15}	161	2.4×10^{15}	164	1.4×10^{15}	158	3.3×10^{15}	153	1.4×10^{15}
0.05	185	1.5×10^{16}	181	4.5×10^{16}	175	5.5×10^{16}	170	6.9×10^{16}	158	6.9×10^{16}
0.10	195	3.6×10^{17}	188	5.1×10^{17}	183	6.1×10^{17}	177	7.2×10^{17}	172	7.5×10^{17}
0.20	198	3.9×10^{17}	187	6.2×10^{17}	182	6.5×10^{17}	175	7.0×10^{17}	171	7.4×10^{17}
0.30	196	3.7×10^{17}	188	5.8×10^{17}	185	7.8×10^{17}	174	7.1×10^{17}	171	7.5×10^{17}
0.40	197	4×10^{17}	186	6.6×10^{17}	184	6.9×10^{17}	175	7.1×10^{17}	170	7.3×10^{17}
0.50	199	4.1×10^{17}	188	6.3×10^{17}	187	6.5×10^{17}	173	7.3×10^{17}	169	7.3×10^{17}
0.60	198	4.2×10^{17}	186	6.5×10^{17}	181	7.5×10^{17}	176	7.6×10^{17}	172	7.4×10^{17}
0.70	195	3.5×10^{17}	187	4.4×10^{17}	184	6.6×10^{17}	177	7.6×10^{17}	171	7.4×10^{17}
0.80	197	3.8×10^{17}	190	5.2×10^{17}	188	5.9×10^{17}	178	7.7×10^{17}	172	7.5×10^{17}
0.90	237	8.7×10^{17}	221	8.2×10^{17}	214	8.6×10^{17}	209	9.8×10^{17}	199	9.8×10^{17}
Average Values (α =0.2-0.8)	197	3.9×10^{17}	188	5.7×10^{17}	184	6.8×10^{17}	176	7.4×10^{17}	171	7.5×10^{17}

Table (3): Kinetic parameters for pyrolysis of PVC and NiO/PVC using different calculation methods.

Material	Friedman Analysis		Coats-Redfern Analysis		Nth-order Arrhenius		Average	Values
	E_a (kJ mol^{-1})	A(min^{-1})	E_a (kJ mol^{-1})	A (min^{-1})	E_a (kJ mol^{-1})	A (min^{-1})	E_a (kJ mol^{-1})	A (min^{-1})
PVC	197	3.9×10^{17}	193	4.1×10^{17}	191	4.3×10^{17}	198.3	4.6×10^{17}
PVC+H$_4$	188	5.7×10^{17}	185	6.9×10^{17}	184	7×10^{17}	185.6	6.5×10^{17}
PVC+N$_3$	184	6.8×10^{17}	181	7.1×10^{17}	178	7.5×10^{17}	181	7.1×10^{17}
PVC+H$_1$	176	7.4×10^{17}	175	7.5×10^{17}	173	7.7×10^{17}	174.8	7.5×10^{17}
PVC+N$_1$	171	7.5×10^{17}	167	7.8×10^{17}	165	7.9×10^{17}	167.6	7.6×10^{17}

Inspection of **Table (2)** shows that the values of E_a and A calculated by using different methods are comparable, which indicates that the kinetic parameters thus obtained are reasonable. The activation energy can provide reasonable information about critical energy needed to start the decomposition reaction of the PVC. Hence, a reduction in the activation energy can be directly correlated to the catalytic activity of the PVC. This may be attributed to some solid reactions that can be occurred on the solid surface of catalytic materials. To sum up, the efficiency for the catalysis process of the first step increases according to surface area of NiO due to decreasing their particle size. The bigger specific surface area of the catalyst provided more contact sites for the reactants and also pathways for gas product to evolve out, thus promoting the overall decomposition of PVC, by occurring at lower temperatures.
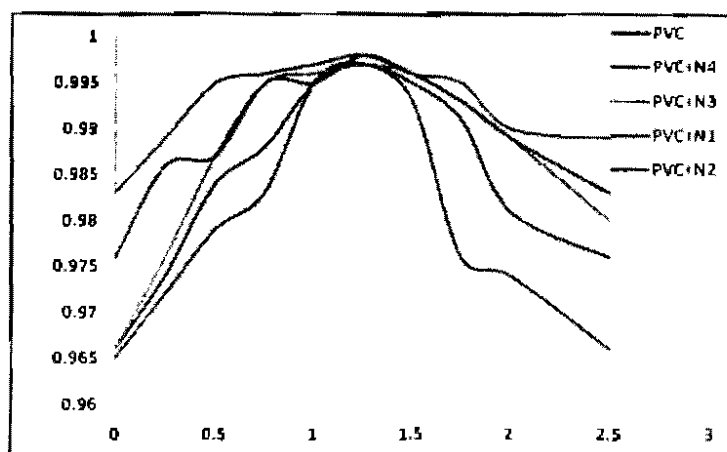
Fig. (2). R^2-n values for Coats-Redfern method for investigated samples.

Table (4). Comparison of pyrolysis data of PVC with and without catalyst.

Sample	1st Stage	2nd Stage	3rd Stage
	T_i (C)	T_i (C)	T_i (C)
PVC	214	336	463
PVC+N_4	209	330	459
PVC+ N_3	205	325	453
PVC+ N_1	201	320	449
PVC+N_2	194	316	442

Mechanism of pyrolysis:

PVC is considered to follow a more complication scheme of reactions involving sets of parallel and consecutive reactions with an intermediate solid which undergoes further decomposition. This was proposed by Marcilla and Beltran [**Marcilla** *et al.*, **(1995)**] who used a three-consecutive-reactions scheme to describe the first two stages of PVC weight loss decomposition in nitrogen atmosphere based on the single ion current (SIC) analysis from Ballistreri et al. [**Ballistreri** *et al.*, **(1980)** Marcilla and Beltran [**Dileka** *et al.*, **(2011)**]used that model to simulate the two-stage weight loss TG curves measured during PVC pyrolysis. Generally, the pyrolysis can be summarizing this in the following scheme of reactions:

$$k_1 \nearrow G_2$$
$$PVC$$
$$k_2 \searrow PVC^*$$
$$k_3 \nearrow G_3$$
$$k_4 \searrow R_s$$
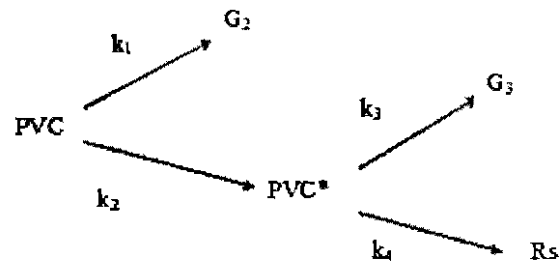
PVC* and R_s represent the resin intermediate and residue, respectively, and G_1 and G_3 represent the gases evolved from the different reaction pathes. k_i represents the rate constant for each individual path (i) . This scheme of reaction, and all derived from it in the present work, cannot be considered as mechanistic, but only as macroscopic representation of the overall processes.

CONCLUSIONS

To enhance the performance of PVC pyrolysis, nano-NiO particles were used as catalysts in pyrolyzing PVC in TG. Meanwhile, evaluation of the catalytic activity of nano-NiO particles in the pyrolysis of PVC was carried out in comparison with that of micro-NiO, in the same conditions. The results indicated that the initial temperaturesof PVC decomposition in the presence of micro- and nano-NiO was lower than that of pure PVC. The acceleration pyrolysis process according the TG curves follows the sequence $PVC/N_2 > PVC/N_1 > PVC/N_3 > PVC/N_4 > PVC$. The kinetics of the pyrolysis of PVC has been investigated under non-catalyzed and catalyzed conditions using different calculation procedures. The pyrolysis kinetics for the first stage thermal decomposition of PVC in presence and absence of NiO catalyst remained unaltered. By means of TG data, an apparent energy of activation E_a of 198.3 kJ mol^{-1}, a pre-exponential factor of 4.6×10^{17} min^{-1} and an apparent order of reaction 1.25 is determined for the non-catalyzed reaction. The order values excellently agree with those of catalyzed reactions. In particular, nano-NiO particles demonstrated a more effective catalytic effect in PVC pyrolysis when compared with micro-NiO particles. The main conclusion, which can be drawn from the kinetic data, is that the NiO accelerates the decomposition of PVC with increasing the surface area of the catalyst.

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دراسة حركية علي التحلل الحرارى للبولى فينيل كلوريد بإستخدام أكسيد النيكل النانو مترى

أ/د وفاء بيومى، أ/د ابراهيم سيد أحمد ، أ/د عبدالحميد البليهى ،

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تم دراسة التحلل الحراري للبولي فينيل كلوريد بإستخدام عامل حفاز وبدون أستخدام
عامل حفاز .كما تم دراسة الثوابت الحركية لعملية التحلل بإستخدام نماذج حركية متعـــددة .
وقد تبين أنه عند استخدام أكسيد النيكل النانو متري نقل درجه الحرارة الازمة لعملية التكسير
عنه عند إستخدام أكسيد النيكل في الحجم العادي ، وكان ترتيب النتائج كالأتي:-
$$PVC/N_2 > PVC/N_1 > PVC/N_3 > PVC/N_4 > PVC$$
وتم حساب الثوابت الحركية للتحلل الحراري في الخطوة الاولــى لمنحنـــي (TG)
فكانت طاقة التنشيط (E_a) تساوى ١٨٩,٣ ك.جول لكل مول . والمعامـــل الحركـــي (A)
تساوى 4.6×10^{17} لكل دقيقه . وأوضحت النتائج ان أكسيد النيكل في الحجم النانو مترى له
تأثير فعال علي تكسير البولي فينيل كلوريد.