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Simulation of the Kinetics of Heterogeneous Oxidation of n-Heptane by Oxygen

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Abstract

The catalytic reaction of n-heptane (n-C_7H_{16}) oxidation with molecular oxygen has been studied. Various compositions of the polymer catalyst Mn-P4VP/MBAA (where Mn-P4VP is manganese-immobilised poly-4-vinylpyridine and MBAA is N,N′-methylene-bis-acrylamide) containing 2–5 wt% Mn were prepared and tested. The concentration of manganese in the catalyst based on immobilized metal-polymer complexes is within the range of 2–5 wt% Mn. The oxidation reaction was carried out at a ratio of components n-C_7H_{16}/O_2/polymer catalyst with Mn = 1 : 3.38 : 0.003 and time 6 h within the temperature range 303–383 K. The data on the yield of the major products of n-heptane oxidation are presented, taking into account the initial components, catalyst composition, temperature and the time of oxygen contact with the reacting components. It has been established that during the oxidation of n-C_7H_{16} (303–383 K), the yield of alcohols is higher than the yield of other oxidation products. The oxidative conversion of n-heptane increases from 45 to 75 mol% with an increase in temperature in the range of 303–383 K. For the multistage oxidation of n-heptane with oxygen, a kinetic model was selected and considered. On the basis of this model, the reaction rate constants were calculated in the range of 303–383 K considering the degree of heptane conversion. The activation energy of n-heptane oxidation was estimated, taking into account the method of choosing the most plausible parameter and experimental data on n-heptane convection.

Keywords: polymer-metal catalysts, catalytic oxidation, n-C_7H_{16}, n-heptane oxidation kinetics

INTRODUCTION

The mechanism of liquid n-C_6–C_8 low-temperature oxidation has been under investigation for years because of the importance of these hydrocarbons as a primary reference fuel [1–6]. The kinetic features of the oxidation of n-alkane molecules are under increased attention within the studies. The urgency of the problem is also due to the intention to improve the efficiency of diesel engines and to develop new engine technologies [7]. In this case, kinetic data are important to provide low-temperature combustion of reference fuels at temperatures below those commonly studied.

To explain the formation of intermediate compounds in the low-temperature oxidation of propane and n-butane, successive reactions of hydroperoxides were studied [8]. The oxidation of n-heptane (n-C_7H_{16}) diluted with an inert gas was determined to be stoichiometric at low temperatures [9]. In that case, a jet-stirred reactor was used, which can be modelled as a perfect-mixing reactor.

Analysis of these classes of reactions suggests that the mechanism of low-temperature oxidation of alkanes, for example, propane and butane [10], is a complex process. Therefore, it is important to develop the studies of kinetic models for hydrocarbon fuel oxidation [11, 12]. There are only a few experimental studies of the low-temperature oxidation of n-C_6–C_8 with species analysis. For instance, authors [13] studied the low-temperature oxidation of n-heptane in a pressurized-flow reactor (at 8 atm), where the temperature coefficient exhibited strongly negative behaviour. The products were carbon oxides, cyclic ethers (*cis*- and *trans*-2-methyl-5-ethyltetrahydrofuran, 2-propyltetrahydrofuran, and 2-methyl-4-propyloxetane), olefins (ethylene, propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, *cis*- and *trans*-2-heptene, and *trans*-3-heptene), and aldehydes (acetaldehyde, propanal, acrolein, butanal, and pentanal).

An experimental study of n-heptane oxidation in a rapid-compression machine was conducted by the authors [14]. They measured ignition delay times in stoichiometric n-heptane – air mixtures at temperatures ranging from 600 to 900 K and at high pressure (3–9 bar).

It has been established, in particular in the above-cited studies, that stoichiometric equations do not reflect the actual progress of the process and may be referred to as an expression depicting the general result of several stages. In this case, the mechanism of a chemical reaction is a set of individual stages: the initial n-alkane gets split to form alkyl radicals, and these radicals add to molecular oxygen to form peroxyalkyl radicals ($ROO^\bullet$), which then isomerise into hydroperoxyalkyl radicals ($QOOH^\bullet$, $Q = C_nH_{2n}$) by the intramolecular transfer of H atom. At a next stage, $QOOH^\bullet$ radicals add again to molecular oxygen (this is called the second addition) to form $OOQOOH^\bullet$ radicals. The $OOQOOH^\bullet$ radicals isomerise and readily decompose to form ketohydroperoxides. This process goes on until the final products are formed. In these successive reactions, in particular, with the participation of carbonyl hydroperoxides, oxygenated compounds are formed. These include organic acids and diones, detected experimentally [15, 16].

In heterogeneous reactions, the factors affecting the rates of chemical transformations are more complex. These factors are: 1) the nature of reagents, 2) concentration, 3) temperature, 4) pressure (for gases), 5) catalyst, 6) the particle size of reactants (for solids).

Elaboration of kinetic models relies on the adequate understanding of the reaction mechanism that occurs at a low temperature. The purpose of the work is to study the oxidation of n-C_7H_{16} in the presence of a manganese-polymer catalyst and to apply the appropriate kinetic model to the process. Additionally, attention was paid to the identification and quantification of reaction products, such as alcohols, aldehydes, and ketohydroperoxides.

EXPERIMENTAL

The effect of Mn-P4VP and Mn-P4VP/MBAA catalysts (where Mn-P4VP is manganese-immobilised poly-4-vinylpyridine and MBAA is N,N′-methylene-bis-acrylamide) on the oxidation of n-C_7H_{16} with oxygen was studied in a flow reactor. The results were described in our previous works, and a brief description can be found in [17–19].

In order to obtain immobilized metal-polymer complexes (MPC), $MnCl_2 \cdot 4H_2O$ salt solutions were added into the ethanolic solutions of quaternised P4VP samples. To restore Mn(II), the redox agent $NaBH_4$ was added to the obtained solutions. The immobilization of the polymer P4VP with manganese was carried out in two ways: 1) by adding a solution of manganese salt to a cross-linking agent in an ethanolic solution of P4VP; 2) by adding a solution of manganese salt after the cross-linking agent MBAA in the ethanolic solution of P4VP.

To determine the properties of the prepared catalysts, the following methods were used: X-ray phase analysis (XRD; D2-Phaser Bruker diffractometer), IR spectroscopic analysis (FTIR spectroscopy Nicolefisio VSA), scanning electron microscopy (SEM and EDS on Sigma VP, Carl Zeiss Jena) [17–19].

The oxidation of n-heptane was carried out at the molar ratio of n-$C_7H_{16}/O_2 = 1 : 3.38$. The temperature was varied in different experiments within 303–383 K at atmospheric pressure. The reactor was charged with n-heptane (5 mL) and Mn-P4VP or Mn-P4VP/MBAA catalyst (0.8 cm^3). The molar ratio of n-C_7H_{16} to catalyst was 0.038 : (0.0012–0.006). The reactor was placed on a heated MS-5 magnetic stirrer. Data identification was carried out by gas chromatography using Agilent 7890B GC with an HP-5 column; the flow rate of carrier gas (H_2 and N_2) was 1.2 mL/min, and the pressure was 37.30 Pa.

RESULTS AND DISCUSSION

Studies of the kinetics of n-C_7H_{16} oxidation show stable catalytic activity and high selectivity

TABLE 1

Results of the tests of non-cross-linked and cross-linked metal-polymer catalysts in the oxidation of *n*-heptane at 313 K

No.	Polymer catalyst composition, wt% Mn	Heptane conversion, ξ, %	The yield of reaction products, wt%						
			C_7H_{16}-1-ol	C_7H_{16}-2-ol	C_7H_{16}-3-ol	C_7H_{16}-4-ol	Heptanal	Heptanone	
								4, 3	2
1	2%Mn-P4VP	10.3	–	4.2	5.8	0.3	–	–	–
2	5%Mn-P4VP	13.2	–	5.8	6.6	0.8	–	–	–
3	2%Mn-P4VP /MBAA*	23.2	1.4	7.3	8.6	3.4	–	0.9	1.6
4	5%Mn-P4VP /MBAA*	36.1	2.9	9.4	10.8	5.3	1.2	2.6	3.9

* Cross-linked metal-polymer catalysts.

Notes. 1. P4VP – poly-4-vinylpyridine; MBAA – N,N′-methylene-bis-acrylamide. 2. Molar ratio of reagents *n*-C_7H_{16}/O_2/polymer catalyst with Mn = 1 : 3.38 : 0.003; time 6 h.

with respect to manganese-immobilized poly-4-vinylpyridine (Table 1).

Manganese in the composition of oxidation catalysts promotes an increase in the activity of Mn-P4VP/MBAA systems, probably due to a change in the activation of C–H bonds by Mn ions in the redox centres of the catalyst.

These experimental results were used to aid in the development and validation of a detailed kinetic model. Our experiments on heptane oxidation show that the model we used earlier for studying the kinetics of *n*-alkane oxidation [19] makes it possible to determine the kinetic parameters also for heptane oxidation.

The basic postulate of chemical kinetics is known to characterise the dependence of reaction rate (v_r) on the concentrations of reagents ([A], [B], *etc.*). It is assumed that the rate of a chemical reaction at a constant time (t) is directly proportional to the product of the concentrations of interacting reagents. Some numerical values of reagent concentrations are determined empirically. In other words, the kinetic equation is written as follows: $v_r = k_v[A]^m[B]^n$, where k_v is the reaction rate constant, m is the reaction order for substance A, n is the reaction order for substance B.

Within the framework of the principle of independence of chemical reactions, we consider the kinetics of complex reactions that include several elementary stages. Let us assume that several simple reactions take place in the system, and each of them obeys the basic postulate of chemical kinetics, independently of other reactions.

When studying chemical reactions, in particular the oxidation of heptane, it is necessary to know which products (C, D, ...) are formed from the reactants (A, B, ...), as well as the stoichiometric coefficients (a, b, c, d, ...) in the equation of oxidation. The reaction we considered was complex, and to predict the dependence of its rate on the concentration of reagents, it is not enough to know the chemical equation. One should also have an idea of the elementary stages through which the transformation under study is carried out. According to the kinetic mechanism, we will take this complex chemical reaction in general terms as competing (sequential and/or parallel) reactions.

Consider a sequential reaction consisting of two monomolecular stages: $S \xrightarrow{k_1} X \xrightarrow{k_2} P$. Here S is the initial substrate (A, B, ...), P is the final products (C, D, ...), k_1 and k_2 are reaction rate constants, and X is the intermediate products. Consider the kinetics of this reaction based on the law of mass action. Then a system of three differential equations may be written for the rates of simple reactions:

$$\frac{dc_S}{dt} = -k_1c_S$$
$$\frac{dc_X}{dt} = +k_1c_S - k_2c_X \tag{1}$$
$$\frac{dc_P}{dt} = k_2c_X$$

where c_S, c_X, c_P are the concentrations of substances S, X, P, respectively.

For an adequate description of oxidative reactions involving *n*-alkanes, it is necessary to use the decomposition of a complex reaction into partial ones: to identify individual intermediate substances, to consider the stages participated by these substances at different temperatures relying on quantum chemical calculations, to draw up detailed schemes of target chemical transformations. In other words, the model scheme is the beginning for constructing a real kinetic model of the generalised mechanism of a catalytic reaction, which is carried out taking into account the kinetic parameters of individual stages of partial reactions [20].

The nature of unstable intermediate products has not been determined by us either. In other words, determining the true rate (or average rate) of the catalytic oxidation of n-heptane is another task.

The rate constant (k) is known to be a constant value (at T (temperature) = const), and it does not depend on the concentrations of reagents. It is determined by the nature of the reactants and depends on the temperature. With this in mind, the value of k was estimated through the experimentally determined conversion (ξ, %) of heptane upon oxidation with oxygen.

Taking into account the above, the calculations of the rate constant of the heptane oxidation reaction were carried out within the framework of the kinetic model given in [19]. During the oxidation of n-heptane to various products, the yield, selectivity, and conversion were determined experimentally using known methods [19, 20–26]. The kinetics of the catalytic oxidation of n-heptane to target products, in particular alcohols, was studied in a flow reactor.

A reactor shaped as a tube of constant cross section with a constant volume was used for this purpose. The mixture was fed into the reactor at the flow rate of 10 mL/min. The activity of the catalyst was evaluated by the conversion of n-heptane in the products at different temperatures. The temperature was raised stepwise with a step of 10 °C. Before the start of the process, catalysts were loaded into the reactor in the amount of 0.8 cm^3. The conversion was determined under steady-state conditions.

The conversions (ξ, %) of C_7H_{16} and O_2 were determined from the ratios:

$$\xi(C_7H_{16}) = \frac{([C_7H_{16}]_{in} - [C_7H_{16}]_{out})}{[C_7H_{16}]_{in}} \cdot 100\ \%$$

$$\xi(O_2) = \frac{([O_2]_{in} - [O_2]_{out})}{[O_2]_{in}} \cdot 100\ \%$$

based on the initial and final concentrations of heptane and oxygen at the inlet ($[C_7H_{16}]_{in}$ and $[O_2]_{in}$) and outlet ($[C_7H_{16}]_{out}$ and $[O_2]_{out}$) of the reactor. In the entire volume of the reactor, the temperature was maintained constant. The conditions created in the reactor ensured that the amount of heat released or absorbed was small, and there were no temperature gradients.

Taking into account the residence time of the mixture of initial components in the reactor, we studied the kinetics of n-heptane oxidation with oxygen. In this case, in the temperature range of 303–383 K, the selectivity for the formation of alcohols is below 10%. In the oxidation of C_7H_{16}, the 5%Mn-P4VP/MBAA catalyst was more active than other compositions due to the large number of active sites of manganese oxide in it.

The kinetic model was chosen based on the experimental data as follows. When the process takes place in a tubular flow reactor, the system of kinetic equations retains its form if instead of the reaction time t we use the concept of "residence time", which is defined by the expression $t = x/u$ (x is the current coordinate, u is the linear velocity of the gas).

Consider the following case. According to experimental data, the chemical reaction proceeds in a closed volume with a decrease in the number of moles according to the scheme A (n-heptane) + B (oxygen) → C (alcohols). The molar concentrations of the initial substances A (n-heptane) + B (oxygen) change because of chemical interaction, as well as due to a decrease in the density of the mixture. In this case, the simple kinetic model is inapplicable.

Due to competing reactions, the rate constants k had a significant scatter. However, in the studied reactions, an inverse dependence of the total reaction rate on temperature was observed. In this case, the formal scheme $A + B \xrightarrow{k} C$ does not allow us to determine the value of k in the form $k = k_0\exp(-E_a/RT)$, where k_0 is a constant, E_a is the activation energy, R is the universal gas constant, T is the temperature.

Taking into account the foregoing considerations and the multistage nature of heptane oxidation reaction, to determine the reaction constant considering the heptane conversion, we used the previously developed model for estimating the rate constant of the alkane oxidation reaction [19]. In this case, the kinetic constant of the reaction was determined from the conversion of the initial substances ξ according to the ratio:

$$\xi(t) = \frac{A_0 - A(t)}{A_0},\ \xi \in [0, 1] \tag{2}$$

where A_0 is the initial concentration of the substance A, A(t) is the molar concentration of the corresponding substance A at any moments of time (t). The initial concentrations of the initial substances A and B were assumed to be the same $A_0 = B_0$. Then for any values of t we have

TABLE 2

The total rate constants of n-heptane oxidation with oxygen to alcohols at atmospheric pressure, proceeding with the participation of a manganese-containing polymer catalyst

T, K	Q, mol/h	t, min	A_0, mol/m^3	ξ, mole fraction of n-C_7H_{16}	$k \cdot 10^5$, m^3/(mol · min)
303	0.0341	360	38	0.45	0.60
313	0.0327	370	34	0.49	0.76
323	0.0315	379	32	0.52	0.89
333	0.0304	387	28	0.58	1.27
343	0.0289	396	26	0.62	1.58
353	0.0277	407	24	0.65	1.90
363	0.0262	417	22	0.68	2.32
373	0.0251	430	20	0.70	2.71
383	0.0243	437	18	0.75	3.81

Notes. 1. n-C_7H_{16}/O_2/polymer catalyst with Mn = 1 : 3.38 : 0.003 and t = 6 h. 2. Catalyst composition 5%Mn-P4VP/MBAA (Mn concentration 5 wt%). 3. T is the temperature; Q is the volumetric flow rate of the initial mixture at the inlet to the reactor; t is the residence time of the mixture in the reactor.

A(t) = B(t). Taking this into account, the kinetic equation of the initial substance can be written as:

$$\frac{dA}{dt} = -kAB = kA^2, \ A = A(t), \ A(0) = A_0 = \text{const} \quad (3)$$

Integrating equation (3), we obtain

$$A(t) = B(t) = \frac{A_0}{1 + A_0 kt} \quad (4)$$

From equation (4) we find

$$\xi = \frac{A_0 kt}{1 + A_0 kt} \quad (5)$$

Using equation (5), we determined the kinetic constant

$$1 = \frac{\xi}{(1 - \xi)} \cdot \frac{1}{A_0 kt} \quad (6)$$

It should be stressed again here that equations (3)–(6), considered above, refer to our published work [19]. This allows the reader to follow the derivation of the final formula for estimating the rate constant of a complex multi-step oxidation reaction.

When discussing the results above, when varying the rate constant for the model reaction, it was assumed that $A_0 = B_0$. In this case, the stoichiometric coefficients correspond to the stoichiometric amounts of the reacting components. It is assumed that more oxygen does not react with heptane.

However, to obtain the maximum conversion in real catalytic reactions, it was necessary to take an excess oxygen concentration. That is, for the oxidation of heptane with the participation of a catalyst, the concentration of oxygen in the reactions was 3.38 times higher than the concentration of heptane.

Time and temperature (Fig. 1) dependences of conversion in the catalytic reactions of n-hexane oxidation with oxygen are similar to each other.

The results of calculating the rate constant of the reaction proceeding with the participation of a manganese-containing polymer catalyst are presented in Table 2. Here t characterizes the residence time of the mixture (heptane + oxygen) after the establishment of steady mode in the reactor.

Figure 1 shows that the conversion of n-heptane in the catalytic oxidation reaction with oxygen increases with increasing temperature T. In the reactions of heptane oxidation with oxygen involving 2%Mn-P4VP/MBAA (2 wt% Mn) and 5%Mn-P4VP/MBAA (5 wt% Mn) catalytic compositions, heptane conversion is 0.50 and 0.75 mole fractions, respectively.

The high conversion of n-heptane with oxygen, with the participation of a catalyst in the appropriate temperature range, indicates that the rate of the interaction of initial components increases with an increase in the concentration of manganese cation.

The activation energy E_a of the reaction was estimated using the maximum likelihood method. That is, we used the method of estimating an unknown parameter by maximising the likelihood function. The value of E_a was taken as the "most plausible" value of the parameter. Within the framework of the theory of statistical science [27], it has been assumed that the parameter E_a maximises the probability of obtaining a given sample $X = (X_1, ..., X_n)$ in n experiments. This

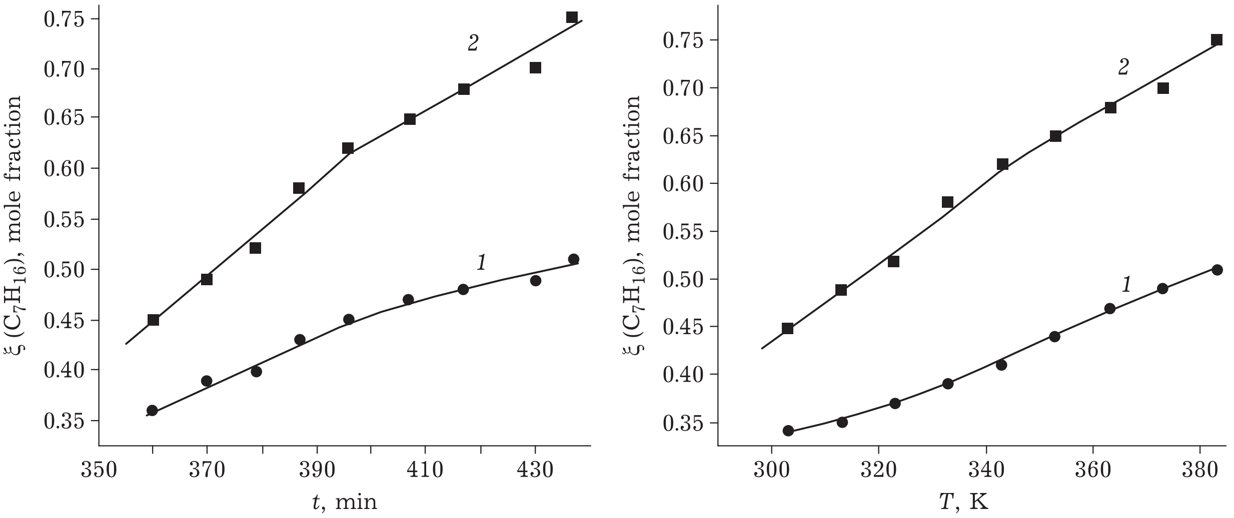

Fig. 1. Time (*a*) and temperature (*b*) dependences of conversion in the catalytic reactions of *n*-heptane (n-C_7H_{16}) oxidation with oxygen. The concentration of Mn in the catalyst sample: *1* – 2 wt% Mn (2%Mn-P4VP/MBAA); *2* – 5 wt% Mn (5%Mn-P4VP/MBAA). For reactions involving catalysts of composition *1* and *2*, n-C_7H_{16}/O_2 = 1 : 3.38.

value of parameter E_a depends on the sample and is the desired estimate.

The likelihood function was calculated using the kinetic formula taking into account *n*-heptane conversion (n-C_7H_{16}/O_2 = 1 : 3.38), and the parameter E_a was estimated from the condition of maximising the likelihood function at a given temperature, pressure, and time of heptane contact with oxygen. The reaction activation energy calculated by this method for the conversion of *n*-heptane, in particular, at $\xi = 70\%$ and 298 K, was $E_a \approx 47$ kJ/mol.

CONCLUSION

The catalytic reaction of *n*-heptane oxidation with molecular oxygen has been studied. Modification of the catalyst composition 5%Mn-P4VP/MBAA containing Mn strongly affects the yield and conversion of *n*-heptane. The introduction of 5 wt% Mn in the polymer composite catalysts increases the yield of alcohols, the conversion of *n*-heptane and catalyst activity.

It has been experimentally established that the yield of alcohols is higher than that of other products of the catalytic oxidation of *n*-heptane within the temperature range of 303–383 K. The conversion of *n*-heptane noticeably increases with increasing temperature. With the participation of a polymer catalyst containing Mn (n-C_7H_{16}/O_2/polymer catalyst with Mn (5%Mn-P4VP/MBAA) = 1 : 3.38 : 0.003, T = 313 K and t = 6 h), the yield of alcohols was, respectively (wt%): for C_7H_{16}-1-ol – 2.9, C_7H_{16}-2-ol – 9.4, for C_7H_{16}-3-ol – 10.8, and for C_7H_{16}-4-ol – 5.3.

The yield and conversion of n-heptane oxidation products depend on the composition of the manganese-containing polymer catalyst, the ratio of the initial components, the temperature and time of contact of the oxygen oxidiser with *n*-heptane. These factors affect the rate constant of the oxidation reaction and determine the form of the temperature dependence of *n*-heptane conversion.

An experimental study of the catalytic oxidation of *n*-heptane showed that the prepared composition of the manganese-containing polymer catalyst with Mn (5%Mn-P4VP/MBAA) makes it possible to increase the conversion of *n*-heptane to alcohol. In the temperature range of 303–383 K, the degree of catalytic oxidative conversion of heptane by molecular oxygen increases from 45 to 75% at a molar ratio of reagents n-C_7H_{16}/O_2/polymer catalyst with Mn (5%Mn-P4VP/MBAA) = 1 : 3.38 : 0.003 and t = 6 h.

Based on the model proposed by us previously for estimating the rate constant of *n*-alkane oxidation reaction, we calculated the rate constants for the oxidation of *n*-heptane with oxygen to alcohols at atmospheric pressure (n-C_7H_{16}/O_2/polymer catalyst with Mn (5%Mn-P4VP/MBAA) = 1 : 3.38 : 0.003 and t = 6 h). For this catalytic oxidation reaction, the calculated value of rate constant varies in the range $k = (0.60–3.81) \cdot 10^{-5}$ $m^3/(mol \cdot min)$ in the temperature range of 303–383 K.

The activation energy of n-heptane oxidation, estimated by the maximum likelihood method, taking into account the experimental data on n-heptane conversion, in particular, for the degree of n-heptane conversion of 70% at 298 K (n-C_7H_{16}/O_2/polymer catalyst with Mn (5%Mn-P4VP/MBAA) = 1 : 3.38 : 0.003, T = 313 K and t = 6 h) was about 47 kJ/mol.

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