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Naphthalene oxidation in supercritical water

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Characteristic features of naphthalene oxidation and the kinetics of naphthalene pyrolysis in supercritical water (SCW) were studied using a batch reactor under isobaric conditions at a pressure of 30 MPa, in the temperature range from 660 °C to 750 °C, and for different levels of oxygen supply, varying from 0 to 2.5 moles of O_2 per mole of naphthalene. The pyrolysis produces benzene, toluene, methane, hydrogen, soot, and carbon oxides. The rate constant for naphthalene pyrolysis in SCW was found to be $k = 10^{12.3\pm0.2}\exp(-E/T)$ s^{-1} where $E = 35400\pm500$ K. For $T > 660$ °C, water participates in the chemical reactions of naphthalene conversion, particularly, in the formation of carbon oxides. The conversion of naphthalene in pure SCW is accompanied by heat evolution. Molecular oxygen oxidizes a part of naphthalene completely, *i.e.*, to CO_2 and H_2O, this reaction being so prompt that in some cases, self-heating of the mixture and thermal explosion in the reactor were observed.

Key words: supercritical water, naphthalene, pyrolysis, oxidation, thermal explosion, reactor, mass spectrometry.

The progress in using water under supercritical conditions ($T > 374$ °C, $P > 22.1$ MPa) as an active medium for partial oxidation of organic compounds in order to convert them into more useful or safe products has stimulated fundamental and applied investigations of the properties of supercritical water (SCW).**[1]** Some parameters such as density, dielectric constant, and ionic dissociation constant change by orders of magnitude following an increase in P and T, thus inducing changes in the mechanisms and kinetics of reactions performed in SCW. Under supercritical conditions, water can dissolve any amounts of oxygen and of weakly polar or nonpolar organic substances.**[2]** The sharp decrease in the ionic dissociation constant for SCW (*e.g.*, to about $2\cdot10^{-20}$ at $T = 500$ °C and $P = 25$ MPa)**[2]** results in ionic reaction mechanisms being replaced by free radical mechanisms. The conversions of hydrocarbon under these conditions yield weakly polar and nonpolar substances such as methane, ethane, benzene, hydrogen, and carbon oxides as the major products.**[3]**

The purpose of this work is to study experimentally the conversion of naphthalene in SCW. Naphthalene was chosen as the object of investigations because of enhanced thermodynamic stability of aromatic compounds, which limits the conversion of natural and synthetic complex organic compounds in the SCW medium.

Experimental

The investigations were conducted in a cylindrical batch reactor made of the 12X18H10T stainless steel. The setup was described in detail previously;**[4]** hence, only the functional diagram is given here (Fig. 1). The following experimental conditions in the reactor were employed: the working pressure was 30±0.1 MPa and the temperature was varied between 660 and 750 °C. The amount of molecular oxygen (β) in SCW varied from 0 to 2.5 moles per mole of naphthalene. The $C_{10}H_8 : H_2O$ molar ratio in the reactor was controlled by adding a definite amount of naphthalene; the density of SCW was taken from a handbook.**[5]** The results given below were obtained with the ratio $C_{10}H_8 : H_2O = 0.07$ mol mol^{-1}. The reaction time (t) was measured starting from the instant of completion of naphthalene feeding into the reactor and ending at the instant the reaction mixture was removed from the reactor into a trap cooled with liquid nitrogen. The experiments were carried out within a time interval of 90—600 s. Supercritical water (either neat or mixed with oxygen) was supplied from a pre-reactor to the evacuated reactor heated to the working temperature ($P \approx 30$ MPa, $T \approx 500$ °C). The amount of water needed to reach $P \approx 30$ MPa at ~ 500 °C in the pre-reactor was determined using the data of Ref. 5 and fed to the pre-reactor at ~20 °C. Oxygen was introduced into the pre-reactor at the same temperature. The amount of O_2 introduced was monitored based on the pressure it created in the pre-reactor. The filled pre-reactor was heated to ≈ 500 °C. After opening the valves between the pre-reactor and the reactor, the temperature in the pre-reactor was varied to achieve the required pressure (30 MPa). Since the pre-reactor volume was 30 times as large as the reactor volume, the temperature change was insignificant. During the reaction, the pre-reactor damped the increase in the reactor pressure. The specified amount of naphthalene was injected into the reactor using a piston, which plugged the reactor inlet. The injection velocity could be varied from a fraction of a second to several minutes. Naphthalene was injected into the upper section of the reactor arranged vertically. The fast dissolution of naphthalene (the duration of

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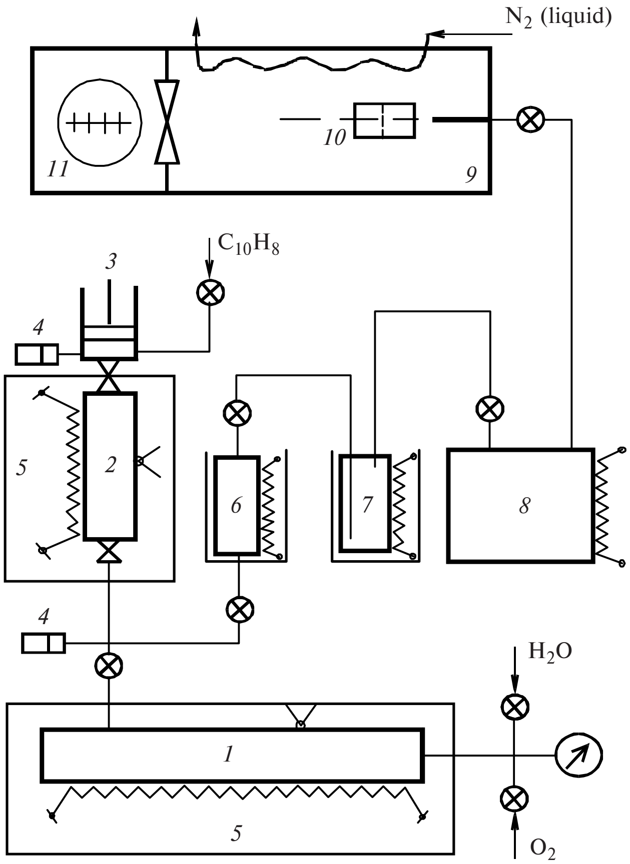

Fig. 1. Schematic diagram of the setup: (*1*) pre-reactor; (*2*) reactor; (*3*) piston; (*4*) strain transducer; (*5*) thermostats; (*6*) trap; (*7*) separator; (*8*) receiver for the gaseous products; (*9*) vacuum chamber; (*10*) ion source of a quadrupole mass spectrometer; (*11*) turbo-molecular pump.

dissolution is estimated to be ~1 s) was promoted by free convective stirring with downward migration of the denser naphthalene. Both the reactor and the pre-reactor were maintained at a constant temperature using baths filled with emery powder. The temperature was measured by thermocouples and maintained to an accuracy of at least ±1 °C. The pressure was measured with diaphragm strain transducers in the 1—40 MPa range with an accuracy of 0.25%. The reaction products were analyzed using a MS-7303 quadrupole mass spectrometer located in a high-vacuum chamber. The reaction products traveled to the mass analyzer *via* the following route: reactor → trap → cryogenic separator → receiver → vacuum chamber → ion source of the mass spectrometer. The gases under analysis flew out of the heated receiver (≈120 °C) into the high-vacuum chamber. A molecular beam was formed from the gas stream by diaphragms;**[6]** the beam crossed the ion source of the mass spectrometer. The quantitative composition of the reaction products was determined from the mass spectra.**[3,4]**

Results and Discussion

The analysis of the gaseous products formed upon naphthalene conversion in SCW showed the presence of a narrow range of compounds, namely CH_4, benzene and toluene (a very small amount), H_2, carbon oxides, and unreacted naphthalene ($C_{10}H_8$). Determination of the quantitative composition posed no difficulties because the molecular ion peaks of these compounds do not overlap and the ionization cross-sections are known.

After removal of the vapor—gas mixture and cooling, the reactor was freed from the solid residue insoluble in organic solvents. The elemental composition of the residue was determined by weighing the products of complete combustion of this material in an O_2 flow in a quartz reactor. The C : H molar ratio in the residue was about ~2. (Hereinafter, carbon in the residue will be referred to as soot and, for a more convenient comparison of soot with other reaction products, its amount will be conventionally expressed in moles of the C_{10} cluster.)

Some of the results of analysis of the products of naphthalene conversion in SCW are plotted as dependences of the proportion of each component (N) on the proportion (β) of O_2 in SCW at 710 °C (Fig. 2) and on the reaction temperature (T) for $\beta = 2.1$ (Fig. 3). The molar amount of each substance is referred to the molar amount of naphthalene injected into the reactor. The change in the amount of water due to the reaction was calculated from the oxygen balance before and after the reaction.

Figure 2 demonstrates that for $\beta = 0$, *i.e.*, in the absence of O_2, the reaction products contain carbon

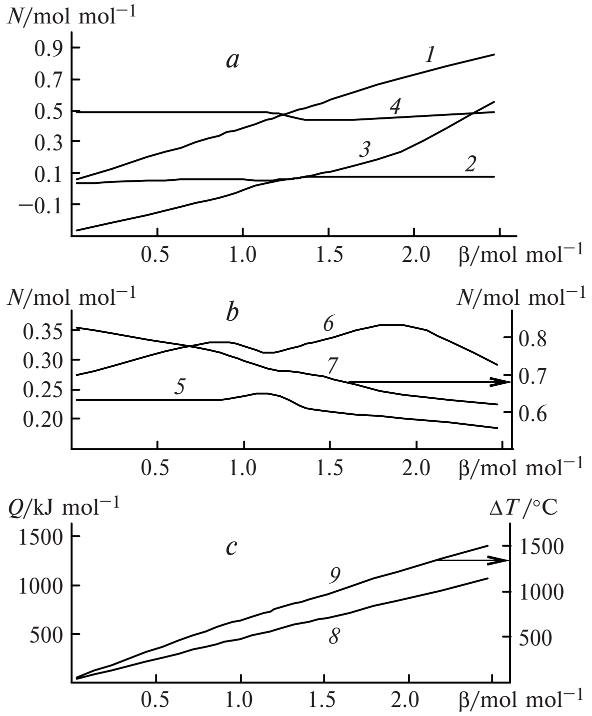

Fig. 2. Effect of the amount of molecular oxygen (β) in the reactor on the proportions (N) of some products of naphthalene conversion (*a*, *b*), on the heat of the reaction (Q, *8*) at 710 °C, and on the increment of the temperature of water (ΔT, *9*) (*c*). Composition of the reaction products: CO_2 (*1*), CO (*2*), H_2O (*3*), soot (*4*); H_2 (*5*), CH_4 (*6*) and naphthalene (*7*).

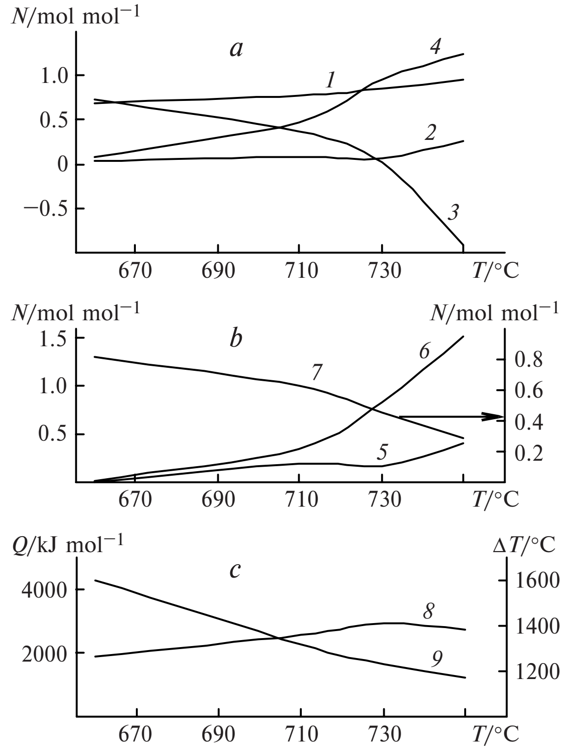

Fig. 3. Effect of the reactor temperature on the proportions (*N*) of some products of naphthalene conversion (*a*, *b*), on the heat of the reaction (*Q, 8*), and on the increment of the temperature of water (ΔT, *9*) (*c*) at $\beta = 2.1$. Composition of the reaction products: CO_2 (*1*), CO (*2*), H_2O (*3*), soot (*4*); H_2 (*5*), CH_4 (*6*), and naphthalene (*7*).

oxides. This implies that water acts as the source of oxygen atoms, that is, it chemically participates in the conversion of naphthalene. Interestingly, the amount of CO does not depend on β, while the amounts of CO_2 and H_2O increase with an increase in the content of O_2 in the reactor. Hence, in the absence of O_2, carbon dioxide is formed in the reaction of CO with H_2O. Note also that the amount of soot decreases somewhat with an increase in the O_2 concentration. We attribute this to the fact that O_2 rapidly oxidizes completely a part of naphthalene, while soot is formed in a slower process of pyrolysis. The same reasoning is attributable to the data shown in Fig. 3.

At 660 °C, reaction products mainly consist of CO_2 and H_2O, the C : H ratio in them being about the same as in naphthalene (see Fig. 3). Apparently, at $T \leq 660$ °C, the conversion of naphthalene in SCW mainly advances *via* complete oxidation of some of naphthalene by oxygen. As the temperature increases, pyrolysis is accelerated and other compounds appear in the conversion products, in addition to CO_2 and H_2O. The fact that O_2 rapidly reacts with naphthalene to oxidize it completely to give CO_2 and H_2O makes it possible to determine the contribution of pyrolysis to the conversion of naphthalene in SCW. To this end, it is sufficient to subtract the amount of naphthalene oxidized by oxygen from its total amount. The data presented in Fig. 3 were employed to derive the temperature dependence $L(T)$ of the amount of naphthalene decomposed during pyrolysis over a period of 600 s.

The rate of pyrolysis was described by the first-order kinetic equation $dL/dt = -kL$, where k is the rate constant of pyrolysis. The experimental $L(t)$ dependence at 710 °C is described satisfactorily by this equation with $k = 4.0 \pm 0.6 \cdot 10^{-4}$ s^{-1}. The data were processed using the least-squares method. The rate constants k for other temperatures were determined from two points, namely, $t = 0$, where L is equal to the total amount of naphthalene injected into the reactor without taking into account the part oxidized by oxygen, and $t = 600$ s. The resulting temperature dependence $k(T)$ is described adequately by the Arrhenius relation $k(T) = A\exp(-E/T)$ with the constant $A = 10^{12.3 \pm 0.2}$ s^{-1} and with the activation energy $E = 35400 \pm 500$ K (the E/R value is given).

The dependences of the heat of reaction (Q) on β (see Fig. 2) and on T (see Fig. 3) were elucidated from the quantitative composition of the products of naphthalene conversion in SCW. The Q values were calculated from the differences between the heats of formation of the final and initial substances at the reaction temperature.[7] The Q values presented in Figs. 2 and 3 are referred to the amount of naphthalene decomposed. It can be seen from Fig. 2 that even at $\beta = 0$, the conversion of naphthalene in SCW is an exothermic reaction.

Under certain conditions, the heat evolved in the conversion of naphthalene in SCW can raise significantly the temperature of the mixture in the reactor. The calculated dependences of the temperature increments (ΔT) on β and T, related to the heat of reaction in pure SCW, are also presented in Figs. 2 and 3. The ΔT values were found in the adiabatic approximation using reference data on the temperature dependences of the enthalpy of SCW.[5] Estimation of the rate of naphthalene oxidation by molecular oxygen in SCW based on experimental data for benzene[8] (no data for naphthalene are available yet) showed that, upon fast (not longer than 10 s) injection of naphthalene into the reactor under conditions of our experiments, the criterion of thermal explosion[9] is attained at $\beta = 2$ for $T = 730$ °C. We observed the thermal explosion effect resulting in ejection of some of the material from the reactor to the pre-reactor. An insignificant self-heating of the reaction mixture was also detected from an increase in the content of methane in the reaction products. It can be seen from Fig. 3 that the methane content in the products is strongly dependent on the temperature. To prevent self-heating of the mixture in the reactor, naphthalene was added slowly (over a period of at least 20 s).

Generally, our investigation showed that at $T \geq 660$ °C, water having supercritical parameters participates chemically in the conversion of naphthalene in the absence of molecular oxygen. The reaction gives carbon oxides, soot, molecular hydrogen, methane, benzene, and toluene. The introduction of O_2 does not influence the chemical composition of the reaction products because oxygen is consumed rapidly and almost completely for oxidation of some of naphthalene to CO_2 and H_2O. The quantitative composition of the products of naphthalene conversion even in the absence of molecular oxygen implies an exothermic reaction. Under certain conditions, the addition of oxygen to SCW initiates the thermal explosion in the reactor bulk.

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