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Kinetics of Oxidation of Lower Olefins with Fe(III) Aqua Ions in the Presence of the $Pd/ZrO_2/SO_4$ Precatalyst in a Chloride-Free System

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Abstract—The kinetics of oxidation of ethene, propene, and 1-butene with Fe(III) aqua ions to the corresponding carbonyl compounds in the presence of the 1% $Pd/ZrO_2/SO_4$ precatalyst in aqueous perchloric acid at 40–80°C was studied. The oxidation rate increases in the order $C_2H_4 < C_4H_8 < C_3H_6$ and with increasing catalyst weight and in the acid and Fe(III) concentrations; it is independent of the olefin pressure. The ethene oxidation rate is described by the Michaelis–Menten equation. In the case of 1-butene, the reaction is accompanied by migration of the double bond with the formation of 2-butene.

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Liquid-phase oxidation of unsaturated hydrocarbons to the corresponding carbonyl compounds in the presence of a Pd-containing catalyst is of basic and applied importance, and studies of these reactions remain urgent [1–8].

In [9, 10] we proved formation of palladium nanoparticles with a mean size of 5 nm and suggested that these particles play a key role in the oxidation of olefins with Fe(III) in an aqueous chloride-free system in the presence of both homogeneous [Pd(II) tetraaqua complex] and heterogeneous ($Pd/ZrO_2/SO_4$) catalysts. In this study we examined the kinetics of catalytic oxidation of ethene, propene, and 1-butene with Fe(III) aqua complex under the action of the $Pd/ZrO_2/SO_4$ precatalyst [reaction (1)]:

$$H_2C{=}CHR + 2Fe(III) + H_2O \xrightarrow{Pd/ZrO_2/SO_4} CH_3C(O)R + 2Fe(II). \tag{1}$$

The kinetic curves of the oxidation of ethene, propene, and 1-butene are shown in Fig. 1. In all the cases, the reaction has an induction period in which the catalytically active palladium nanoparticles, detected and described in [10], are formed. The duration of the induction period depends on the initial concentrations of the components and the temperature. When studying the effect of the system components on the reaction kinetics, we took as a criterion the maximal reaction rate attained immediately after the completion of the induction period.

Figure 1 shows that the maximal rate of olefin oxidation with Fe(III) aqua ions in the presence of $Pd/ZrO_2/SO_4$ increases in the order $C_2H_4 < C_4H_{10} < C_3H_6$, and the rate ratio at 65°C is 1 : 1.4 : 3. The higher rate of the oxidation of propene, compared to that of ethene, is consistent with the increase in the nucleophilic properties from ethene to propene. This fact suggests that reaction (1) involves palladium species in a higher oxidation state. In this case, the rate of 1-butene oxidation should be still higher. However, this is not the case. With 1-butene, the oxidation is accompanied by migration of the double bond with the formation of 2-butene. In particular, at 55°C in

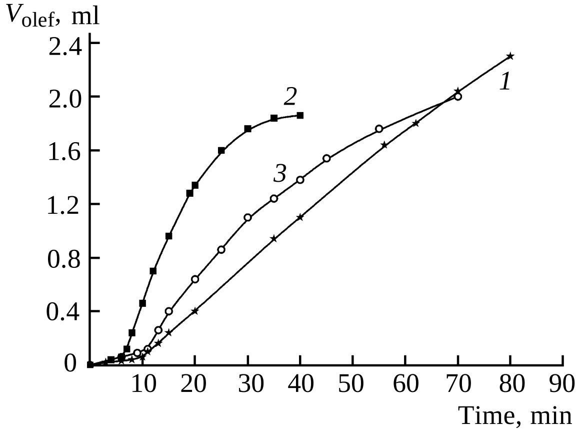


Fig. 1. Kinetic curves of the oxidation of olefins with Fe(III) aqua ions in the presence of $Pd/ZrO_2/SO_4$ (40 mg). $[Fe_{aq}^{3+}]_0$ 0.03 M, 65°C. (*1*) C_2H_4, (*2*) C_3H_6, and (*3*) C_4H_8.

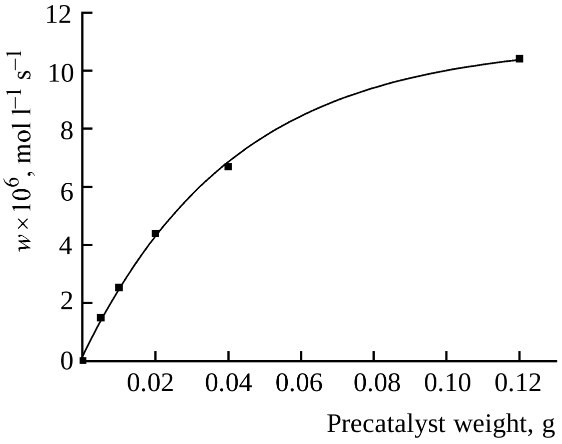


Fig. 2. Initial rate of ethene oxidation by reaction (1) as a function of the precatalyst weight. $[Fe_{aq}^{3+}]_0$ 0.03 and $[HClO_4]$ 0.4 M; $P(C_2H_4)$ 0.1 MPa; 65°C.

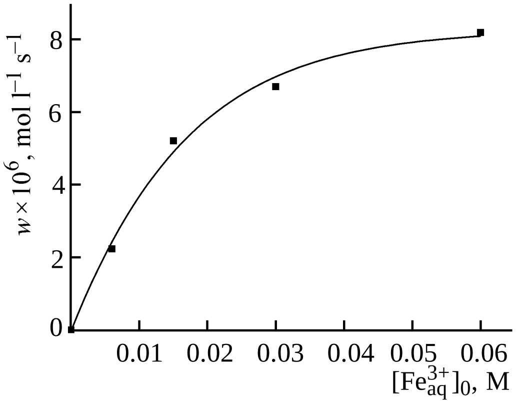


Fig. 3. Initial rate of ethene oxidation as a function of the initial Fe(III) concentration. Precatalyst weight 40 mg; $[HClO_4]$ 0.4 M; $P(C_2H_4)$ 0.1 MPa; 65°C.

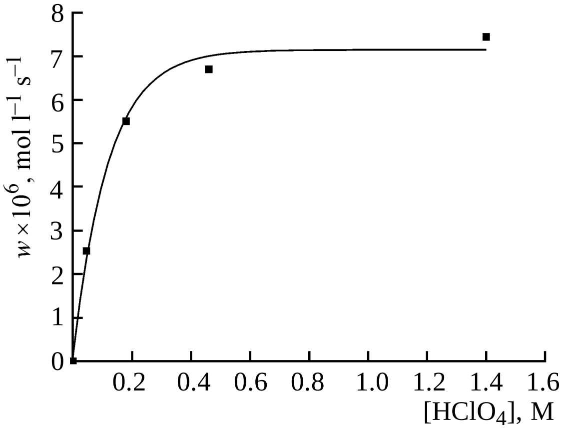


Fig. 4. Initial rate of ethene oxidation as a function of the perchloric acid concentration. Precatalyst weight 40 mg; $[Fe_{aq}^{3+}]0$ 0.03 M; $P(C_2H_4)$ 0.1 MPa; 65°C.

70 min, 30% of 1-butene is converted to 2-butene (10% into *cis*-2-butene and 20% into *trans*-2-butene), and only 3% of 1-butene is oxidized with the formation of methyl ethyl ketone.

We found that 1-butene does not isomerize into 2-butene on sulfated zirconium oxide in aqueous perchloric acid solution in the presence of Fe(III). The migration of the double bond occurs only in the presence of $Pd/ZrO_2/SO_4$ and Fe(III). It is believed that the migration of the double bond in the olefin is catalyzed by palladium in an intermediate oxidation state [5, 11]. The positional isomerization we observed suggests the occurrence of reactions in which Pd(0) from $Pd/ZrO_2/SO_4$ transforms into an intermediate oxidation state catalyzing the isomerization. Partial isomerization of 1-butene into 2-butene apparently explains slower oxidation of butene compared to propene. It is known that 2-butene is oxidized less readily than 1-butene [4, 5].

In this study the majority of kinetic experiments were performed with ethene.

As seen from Figs. 2–4, the dependences of the ethene oxidation rate on the amounts of the precatalyst, Fe(III), and perchloric acid have a complex shape and are described by curves with saturation, which are linearized in the Lineweaver–Burk coordinates as applied to the Michaelis–Menten rate equation.

Unexpectedly, the oxidation appeared to be zero-order with respect to the ethene partial pressure. Apparently, the ethene oxidation step proper is preceded by a slow step of a certain catalytic redox reaction.

With a decrease in the initial partial pressure of ethene, the reaction deceleration with time becomes more pronounced (Fig. 5).

Thus, the rate equation of reaction (1) for ethylene has the form

$$w = k \frac{\mathrm{Pd}}{K' + [\mathrm{Pd}]} \frac{[Fe_{aq}^{3+}]_0}{K'' + [Fe_{aq}^{3+}]_0} \frac{[HClO_4]}{K''' + [HClO_4]} [C_2H_4]^0,$$

where k 3.5×10^{-5} mol l^{-1} s^{-1}; K' 3.8×10^{-4}, K'' 0.03, and K''' 0.1 mol l^{-1} at 65°C; [Pd] denotes the total amount of Pd (moles) in the precatalyst $Pd/ZrO_2/SO_4$ taken for the reaction in the unit volume of the solution.

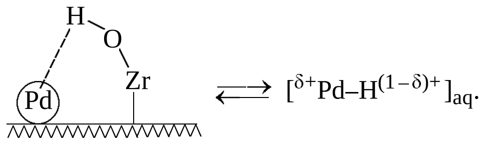
The temperature dependence of the rate constant k is complex. The Arrhenius plot of the ethene oxidation rate has a bend. In the range 40–55°C, the activation energy is 69 ± 7 kJ mol^{-1}, and at 55–75°C, 141 ± 14 kJ mol^{-1}. The bend suggest a change in the structure and energy state of active palladium centers at the corresponding temperature [12]. At higher temperatures (55–75°C), the number of active centers increases, and their potential energy decreases. As a result, the activation energy of the catalytic reaction increases in accordance with the theory of active centers.

The apparent activation energy of the oxidation of propene and 1-butene at 55–75°C is 83 ± 8 and 99 ± 9 kJ mol^{-1}, respectively.

The lack of the influence of the ethene pressure on the oxidation rate does not allow reaction (1) to be considered as a purely heterogeneous reaction involving adsorption of an unsaturated hydrocarbon on the catalyst surface followed by its oxidation. The rate equation of the ethene oxidation suggests that the carbonyl compound is formed from the olefin after the limiting step and that the limiting step is apparently the transfer of palladium particles from the surface of the solid catalyst to solution with the formation of palladium nanoparticles, followed by their oxidation with Fe(III) aqua ions.

The possible transfer of platinum group metals from the finely dispersed state in a metallic catalyst to solution under the action of protons is discussed in [13–15]. Apparently, hydroxonium ions in the reaction solution promote the transfer of palladium nanoparticles from the precatalyst surface to solution, as suggested by an increase in the olefin oxidation rate with an increase in the acid concentration.

In an aqueous medium, Brønsted acid centers are formed on the support surface. Metallic palladium particles interact with such centers, forming an adduct $[Pd–H]^{\delta+}$ [16] in which Pd particles acquire a fractional positive charge, $[Pd_n^{x\delta+}H_x^{(1-\delta)x+}]_{aq}$.



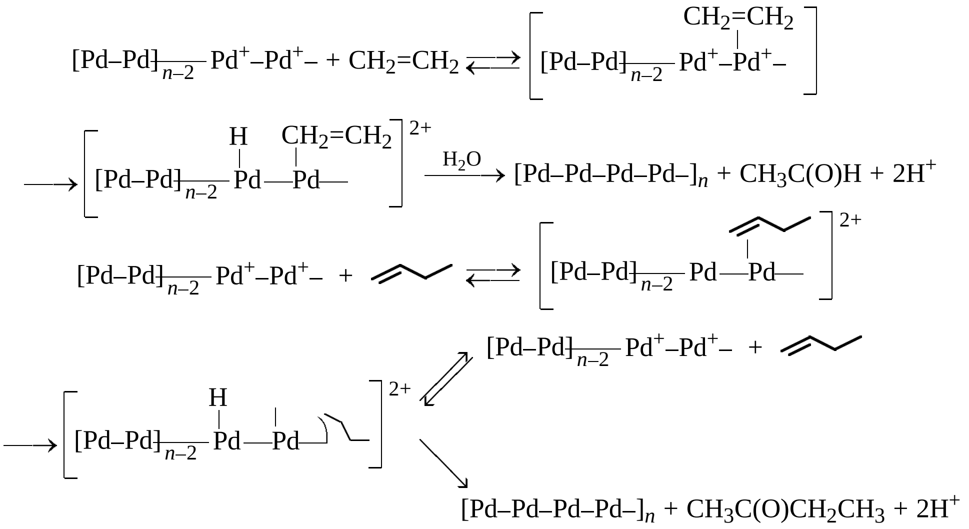
We found previously that palladium particles in the intermediate oxidation state can be oxidized with Fe(III) aqua ions [17, 18]. It is known that the particle size of Pd determines its redox properties [19]. Apparently, in the adduct the palladium nanoparticles exhibit sufficient reducing power to be oxidized with Fe(III) aqua ions with the formation of oxidized palladium species. Data on the partial oxidation of metallic Pd atoms in a Pd cluster with Fe(III) aqua ions with the formation of Pd species in an intermediate oxidation state are reported in [20]. The reaction of the Pd adduct with Fe(III) aqua ions yields Pd species in an intermediate oxidation state, +1:

$$[Pd_n^{x\delta+}H_x^{(1-\delta)x+}]_{aq} + Fe^{3+}_{aq} \rightleftarrows [Pd_{n-1}Pd^{+}]_{aq} + Fe^{2+}_{aq} + H^{+}, \quad (2)$$

$$[Pd_{n-1}Pd^{+}]_{aq} + Fe^{3+}_{aq} \longrightarrow [Pd_{n-2}Pd_2^{2+}]_{aq} + Fe^{2+}_{aq}. \quad (3)$$

In the subsequent process, the olefin is rapidly oxidized on the active center of the $[Pd_{n-2}Pd_2^{2+}]_{aq}$ particles to the corresponding carbonyl compound via formation of a palladium vinyl compound or of a π-allyl complex (in the case of propene and 1-butene).

After reaction (4), the catalytic cycle is repeated.



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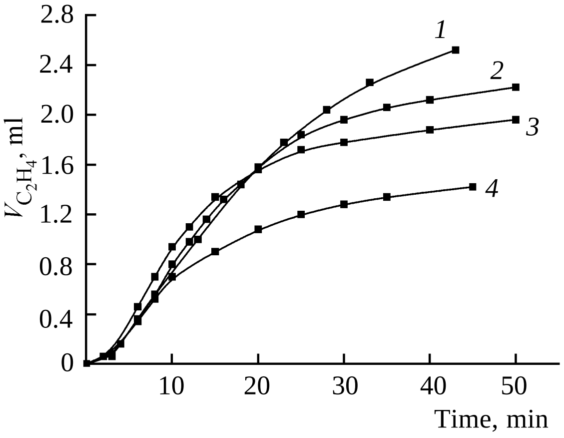

Fig. 5. Influence of the ethene partial pressure on its oxidation. Precatalyst weight 10 mg; $[Fe_{aq}^{3+}]0$ 0.03 and $[HClO_4]$ 0.4 M; 65°C. $P(C_2H_4)$, MPa: (*1*) 0.1, (*2*) 0.05, (*3*) 0.025, and (*4*) 0.015.

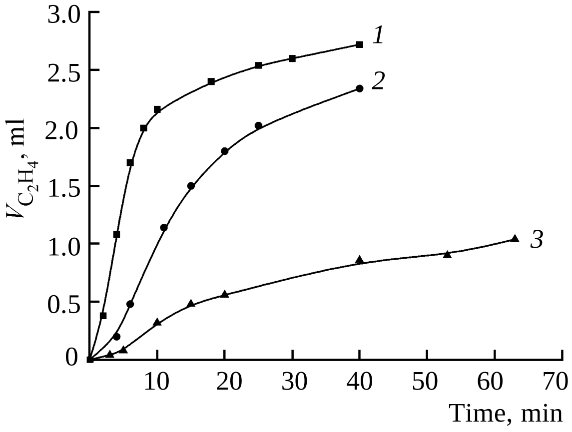

Fig. 6. Influence of the Fe(II) concentration on the ethene oxidation in the system 1% $Pd/ZrO_2/SO_4$–$Fe(III)_{aq}$. Precatalyst weight 40 mg; $[Fe_{aq}^{3+}]_0$ 0.03, $[HClO_4]$ 0.4 M; 73°C. $[Fe_{aq}^{2+}]_0$, M: (*1*) 0, (*2*) 0.03, and (*3*) 0.06.

The oxidation of palladium nanoparticles with Fe(III) aqua ions [reaction (2)] is influenced by the Fe(II) concentration. Addition of Fe(II) aqua ions to the initial reaction system makes the induction period longer (Fig. 6) and decelerates the overall reaction of the olefin oxidation. The maximal oxidation rate is inversely proportional to the initial Fe(II) concentratoin.

Apparently, the effect of Fe(II) is caused by the equilibrium character of the reaction between the Pd nanoparticles and Fe(III) aqua ions. The equilibrium character of reaction (2) is also confirmed by the influence of the initial Fe(III) concentration on the ethene oxidation rate. As the concentration ratio of the arising Fe(II) and remaining Fe(III) reaches a definite value, the reaction always decelerates. In particular, in the oxidation of ethene at 65°C, the Fe(II)/Fe(III) ratio is close to 1 : 2 and is independent of the initial Fe(III) concentration.

The Fe(II) aqua ions arising in the course of the olefin oxidation compete with the unsaturated hydrocarbon for the active Pd center, the competition becoming particularly pronounced at low olefin pressures (Fig. 5). Therefore, the Fe(III) conversion usually does not reach 100%. With an increase in the temperature, the Fe(III) conversion increases. For example, in the ethene oxidation, the Fe(III) conversion was 47% at 50°C and 90% at 75°C.

According to [21, 22], in the presence of Fe(III) aqua ions the formation of palladium π-allyl complexes prevails over the oxidative transformation of olefins into the corresponding carbonyl compounds in the reaction of olefins with Pd(II) tetraaqua complex. Therefore, the formation of π-allyl complexes on active palladium centers in the case of propene and 1-butene can also be responsible for a decrease in the oxidation rate. As seen from Fig. 1, the reaction deceleration observed in the kinetic curves of the oxidation of propene and 1-butene is more abrupt compared to the oxidation of ethene.

We estimated kinetically the steady-state concentration of palladium in solution in oxidation of ethene with Fe(III) in the presence of $Pd/ZrO_2/SO_4$. To this end, we chose as the reference reaction the oxidation of ethene with vanadate ion (VO_2^+) under similar conditions. Preliminary experiments showed that vanadate ion quantitatively oxidized Pd(0) to Pd(II) on contact with $Pd/ZrO_2/SO_4$. Therefore, the oxidation of ethene with vanadate ion in the presence of $Pd/ZrO_2/SO_4$ can be considered as a catalytic reaction with respect to Pd(II). For example, at the initial weight of the $Pd/ZrO_2/SO_4$ catalyst of 1 mg, which corresponds to the 10^{-5} M concentration of Pd(II) in the solution after the oxidation with vanadate ion (0.06 M), the rate of ethene oxidation at 65°C is 7.4×10^{-6} mol l^{-1} s^{-1}. With Fe(III), at its similar initial concentration (0.06 M), the same rate of ethene oxidation is attained with 40 mg of the $Pd/ZrO_2/SO_4$ catalyst. This fact suggests that, in the course of ethene oxidation with Fe(III) aqua ions in the presence of $Pd/ZrO_2/SO_4$, ~2.5% of Pd transforms into the active species.

Thus, the transfer of palladium nanoparticles into solution from the surface of the supported Pd metal catalyst $Pd/ZrO_2/SO_4$, promoted by protons of the medium and acid–base properties of the support, creates conditions for the catalytic oxidation of olefins with Fe(III) aqua ions, similarly to the Wacker process but in the absence of chloride ions.

EXPERIMENTAL

The procedure for preparing the $Pd/ZrO_2/SO_4$ precatalyst was described in [10]. The Pd content in the sample was 1 wt %. Ethene, propene, and 1-butene (Aldrich) were ≥99% pure. Iron(III) was added to the reaction solution in the form of $Fe_2(SO_4)_3 \cdot 9H_2O$ (an aliquot of a solution in perchloric acid). The Pd(II) concentration was determined spectrophotometrically from the intensity of the green color of the complex obtained on adding an excess of a $SnCl_2$ solution to a sample of the reaction solution [23]. The Fe(III) concentration was also determined spectrophotometrically (with sulfosalicylic acid [24]).

The partial pressure of ethene was varied by its dilution with Ar. In all the cases, the total gas pressure was 0.1 MPa.

The kinetic experiment was performed as follows. A weighed portion of $Pd/ZrO_2/SO_4$ was added to a solution of Fe(III) in $HClO_4$ of the required concentration. The volume of the reaction solution was 10 ml in all the experiments. The reaction was performed on a volumetric unit in a temperature-controlled duck-shaped vessel at temperatures from 40 to 80°C with shaking; the reaction progress was monitored by measuring the olefin uptake. In preliminary experiments we determined the shaking frequency above which the reaction rate remained constant, i.e., the reaction was kinetically controlled. For comparison, we also performed test reactions with magnetic stirring at 1200 rpm and obtained similar reaction rates. The oxidation products were extracted from aqueous solutions with chlorobenzene and analyzed by gas chromatography–mass spectrometry (HP-5890GCD instrument equipped with a 30-m HP-5 column).

The products of the positional isomerization of 1-butene were analyzed by ^1H NMR spectroscopy (Bruker DPX-300 spectrometer) upon saturation of the solvent ($CDCl_3$) with the gaseous catalyzate after the reaction completion, and also by gas chromatography–mass spectrometry (Agilent 6890/5973 Network 1000 × 250 × 5 device, determination of the composition of the gas phase in the reactor).

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