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The study of cyclooctene oxidation with molecular oxygen catalyzed by VSi_2

Research Article

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Abstract: The catalytic effect of VSi_2 on initial stages of the liquid-phase oxidation of cyclooctene by molecular oxygen was studied. The vanadium disilicide influences on the oxidation process in the presence of hydroperoxide. VSi_2 takes part in a radical formation stage by catalysis of hydroperoxide decomposition reaction. The catalyst was investigated before and after reaction using FTIR spectroscopy. From the data obtained, the kinetic model of the catalytic oxidation process was proposed and the equation for the reaction rate was derived. The equation has described all observed dependences of reaction rate on the concentration of reactants and content of catalyst.

Keywords: *Oxidation • Catalyst • Oxygen • Kinetics*

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1. Introduction

The O_2 is an inexpensive and ecologically clean oxidant. That is why the reaction of oxidation with molecular oxygen is an attractive process from an economic and ecological viewpoint. Moreover, it is an important process in organic synthesis for obtaining various oxygen-containing compounds – epoxides, acids, alcohols, *etc*., [1-3]. However, direct noncatalytic oxidation of hydrocarbons by molecular oxygen leads mainly to mixtures of various oxygen-containing products and accordingly to a low yield of main product.

The most effective method of increasing the reaction rate and selectivity of desired product formation is application of a catalyst in this process [3-6]. The catalyst can influence on various elementary stages of the oxidation process of hydrocarbons by molecular oxygen: radical formation, chain propagation and termination reactions. It results in changes of the overall oxidation rate as well as the ratio of the reaction products, therefore, increasing the desired product yield. However, some aspects of the mechanism of this interesting reaction are still not clear. Therefore, the investigations of kinetics and mechanism of this process, especially, the mechanism of the catalyst action are important for finding optimum conditions for the production of desired product [3,7,8].

Vanadium containing catalysts are the most active catalysts for the oxidation processes, and widely used in industry [5,9-12]. Great attention is focused on supported vanadium oxide catalysts, which are obtained by supporting vanadium oxide on various surfaces, in particular SiO_2, in order to improve of catalytic performance of V_2O_5. The Si–O and V–O bonds that are present on surface of V_2O_5–SiO_2 catalyst determine the activity of this catalyst. Therefore, it was interesting to investigate the catalytic activity of vanadium and silicon compounds without oxygen in the oxidation reaction.

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During the oxidation reaction, the concentrations of oxidation products increased. Accordingly, observed kinetic regularities of the process can be connected with action not only one of reagents or catalyst, but also with influence of the products formed in the reaction. Investigation of the oxidation process on initial stages eliminated the influence of reaction products on the process. It gives the possibility to investigate the contribution of every component of the reaction mixture, in particular catalyst, in the general process.

Hence, in the present work, we report the investigation of catalytic activity and mechanism of action of vanadium disilicide VSi_2 on the initial stages of the liquid-phase oxidation of cyclooctene by molecular oxygen.

2. Experimental Part

Vanadium disilicide VSi_2 was obtained from Aldrich. Cyclooctene obtained from Acros Organics was additionally distilled before use. Chlorobenzene (Aldrich) was used as a solvent. Molecular oxygen was purified before use. Azodiisobutyronitrile (AIBN) was purified by recrystallization from ethyl alcohol. *tert*-Butyl hydroperoxide (TBHP) was synthesized by the procedure in [13].

The oxidation reaction was performed in a thermostated glass reactor with magnetic stirrer at 90 kPa of oxygen and 353 K. The oxygen absorption was measured with a volumetric device described in [14]. The initial rate of the oxidation reaction was equal to the initial rate of oxygen consumption, which was determined by the extrapolation of the oxygen consumption curve to the initial point of time. The products of cyclooctene oxidation were epoxycyclooctane, 2-cycloocten-1-one, 2-cycloocten-1-hydroperoxide and suberic acid. In the reaction mixture was also presented *tert*-butanol as a product of TBHP decomposition.

The properties of VSi_2 surface were determined by low-temperature (77.4 K) nitrogen adsorption-desorption method using Micromeritics ASAP 2405N analyser. The BET surface area of VSi_2 was 1.8 m^2 g^{-1}, total pore volume 3.8×10^{-3} cm^3 g^{-1}, average pore diameter 86.9 Å.

The IR spectra were recorded on FTIR 1725× (Perkin-Elmer) spectrophotometer using KBr pellets. The measurements were carried out over the 4000–400 cm^{-1} range. The catalyst was stirred at reaction temperature with solution of cyclooctene, TBHP or cyclooctene and TBHP in chlorobenzene. After that the catalyst was separated from the mixture, degassed, pressed with KBr and IR spectrum was recorded.

The products of the oxidation reaction were identified on Hewlett Packard HP 6890 N chromatograph fitted with DB-1 capillary column and on Hewlett Packard HP 5890 II chromatograph with DB-5 ms capillary column and Hewlett Packard HP 5971 mass spectrometric detector. The oven temperature was varied in a temperature-programmed mode within the range of 323–523 K at a rate of 10 K min^{-1}. The carrier gas was helium.

3. Results and Discussion

In the beginning, the oxidation reaction of cyclooctene in the presence and without VSi_2 was carried out in the absence of TBHP or AIBN as homogeneous initiators in the reaction system. It was established that purified and distilled cyclooctene is not oxidized under these reaction conditions for 30 minutes.

Fig. 1 presents the kinetic curves of the oxygen consumption in the process of the oxidation of cyclooctene with molecular oxygen catalyzed by VSi_2 at different concentration of *tert*-butyl hydroperoxide. One can see that the increase in TBHP concentration leads to the increase in the oxygen consumption.

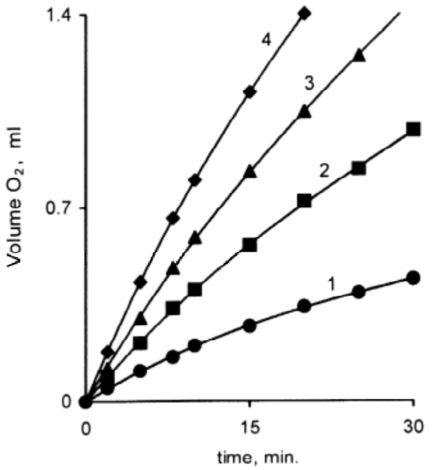


Figure 1. Oxygen consumption kinetics at TBHP concentration: 0.035 (1), 0.07 (2), 0.10 (3), and 0.14 (4) mol L^{-1}. Reaction conditions: [Ol] = 4,1 mol L^{-1}; [Cat] = 5 g L^{-1}.

The data presented in Fig. 2 demonstrate that the dependence of the initial rate (R_{ox}) of cyclooctene oxidation on TBHP concentration is linear. It indicates that the reaction is first order with respect to hydroperoxide. Investigation of influence of partial pressure of oxygen (P_{O_2}) on both catalytic and noncatalytic oxidation process in the presence of TBHP have shown (Fig. 3) that at partial pressure of oxygen higher than 50 kPa the oxidation rate does not depend on the pressure of oxygen.

The kinetic curves of the oxygen consumption at different concentrations of cyclooctene and at different catalyst content are presented in Figs. 4 and 5, respectively. It can be seen, that the oxygen consumption increases with increasing concentration of cyclooctene and catalyst content. From Figs. 6 and 7 it is seen that the dependences of the initial rate of the oxidation of cyclooctene on the cyclooctene (Ol) concentration as well as on the catalyst content are nonlinear and the reaction is less than first order with respect to these components.

This kind of dependence of R_{ox} on [Cat] can deal with participation of vanadium disilicide in chain propagation and termination reactions. In this case, in the presence of another homogeneous initiator of the radical process - AIBN, VSi_2 would also participate in these reactions. However, as it can be seen from Fig. 8, VSi_2 does not influence the process in the presence of AIBN. It was also established that VSi_2 did not influence the rate of decomposition of AIBN. These facts indicate that vanadium disilicide does not influence the processes of chain propagation and termination at initial stages of the process. Consequently, influence of VSi_2 on the oxidation process of cyclooctene deals with the processes in which TBHP takes place.

Results presented in Fig. 7 also show that dependence of the oxidation rate on VSi_2 content does not begin from zero. This noncatalytic component of oxidation process is related to formation of radicals as a result of the noncatalytic decomposition of TBHP [15].

Based on the obtained results as well as data of literature [3,16] and data of our previous works [17,18] the process of cyclooctene (RH) oxidation by molecular oxygen in the presence of VSi_2 and TBHP on the initial stages of the reaction can be described by the scheme that contains radical formation, chain propagation and chain termination reactions:

1) radical formation reactions:

$$\mathrm{TBHP} + \mathrm{TBHP} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Z_1\,; \quad Z_1 + \mathrm{Cat} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Z_2\,;$$

$$Z_1 \xrightarrow{k_n} (CH_3)_3O^{\bullet} + (CH_3)_3OO^{\bullet} + H_2O\,; \tag{1}$$

$$Z_2 \xrightarrow{k_c} (CH_3)_3O^{\bullet} + (CH_3)_3OO^{\bullet} + H_2O + Cat\,. \tag{2}$$

where Z_1 – complex between TBHP molecules; Z_2 – complex of catalyst with two molecules of TBHP; k_n – rate constant of reaction of noncatalytic radicals formation; k_c – rate constant of radicals formation reaction in the presence of catalyst.

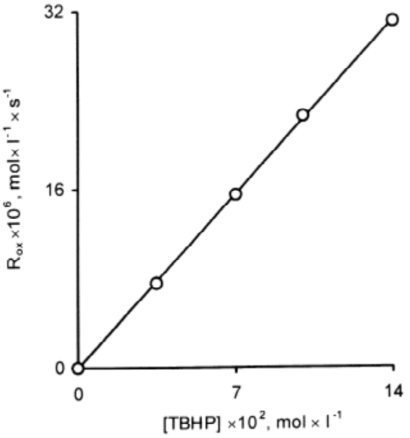


Figure 2. The experimental points, for the data shown in Fig. 1, and theoretically calculated with Eq. 5 dependence of initial rate of cyclooctene oxidation process on TBHP concentration.

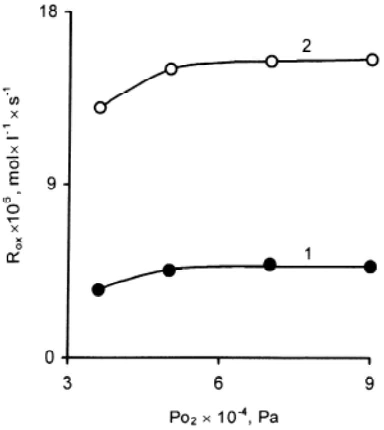


Figure 3. Dependence of initial rate of cyclooctene oxidation on partial pressure of oxygen in noncatalytic (1) and catalytic (2) process. Reaction conditions: [Ol] = 4,1 mol L^{-1}; [TBHP] = 7×10^{-2} mol L^{-1}; [Cat] = 5 g L^{-1}.

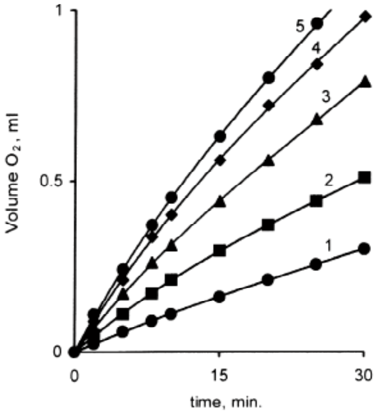


Figure 4. Oxygen consumption kinetics at cyclooctene concentration: 0.46 (1), 1.03 (2), 2.06 (3), 4.1 (4), and 6.9 (5) mol L^{-1}. Reaction conditions: [TBHP] = 7×10^{-2} mol L^{-1}; [Cat] = 5 g L^{-1}.

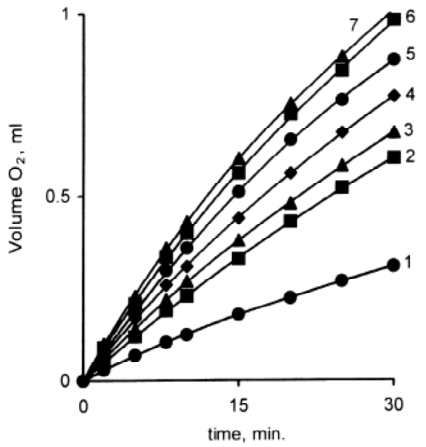


Figure 5. Oxygen consumption kinetics at VSi_2 content: 0 (1), 0.4 (2), 0.75 (3), 1.25 (4), 2.5 (5), 5 (6), and 10 (7) g L^{-1}. Reaction conditions: [Ol] = 4,1 mol L^{-1}; [TBHP] = 7×10^{-2} mol L^{-1}.

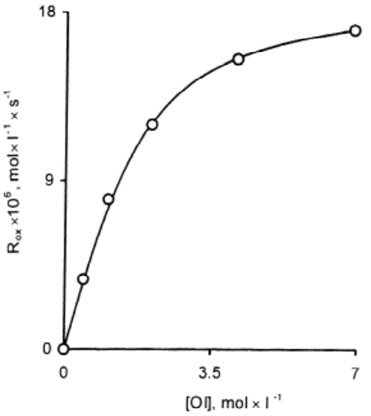


Figure 6. The experimental points, for the data shown in Fig. 5, and theoretically calculated with Eq. 5 dependence of initial rate of oxidation process on cyclooctene concentration.

The data from FTIR investigation, indicates that TBHP can be replaced in complex Z_2 by cyclooctene when the cyclooctene concentration increases (similar process takes place in catalytic epoxidation of 1-octene by TBHP [18] – system with the similar composition). It leads to decrease in amount of catalytic centers responsible for radical formation and can be written as follows:

$$Z_2 + 2Ol \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} Z_3 + 2TBHP \qquad (3)$$

where Z_3 – complex of catalyst with two molecules of cyclooctene.

It is evident that the process described by Eq. 3, has to proceed in two stages:

$$Z_2 + Ol \rightleftarrows Z' + TBHP\,,$$

$$Z' + Ol \rightleftarrows Z_3 + TBHP\,.$$

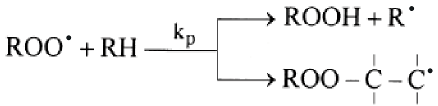
However, with the purpose to simplify the calculations we wrote these two stages as one stage as it is identical from mathematic point of view.

2) chain propagation reactions:

$$(CH_3)_3O^\bullet + RH \rightarrow (CH_3)_3OH + R^\bullet$$

$$(CH_3)_3OO^\bullet + RH \rightarrow (CH_3)_3OOH + R^\bullet$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet$$



$$ROO^\bullet + RH \xrightarrow{k_p} \begin{cases} ROOH + R^\bullet \\ ROO-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}^\bullet \end{cases}$$

3) chain termination reaction:

The fact that the oxidation rate does not depend on the pressure of oxygen at 90 kPa indicates that $[ROO^\bullet] > [R^\bullet]$. Hence, the chain termination reaction can be presented as [3,16]:

$$ROO^\bullet + ROO^\bullet \xrightarrow{k_t} \text{products}$$

According to the above scheme of cyclooctene oxidation, the rate of cyclooctene oxidation (R_{ox}) can be written by the classical equation [3,16]:

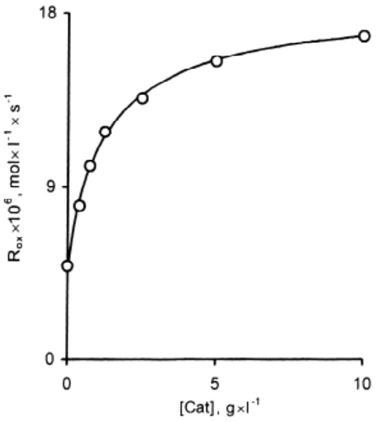


Figure 7. The experimental points, for the data shown in Fig. 6, and theoretically calculated with Eq. 5 dependence of initial rate of cyclooctene oxidation process on content of VSi_2 in the presence of TBHP.

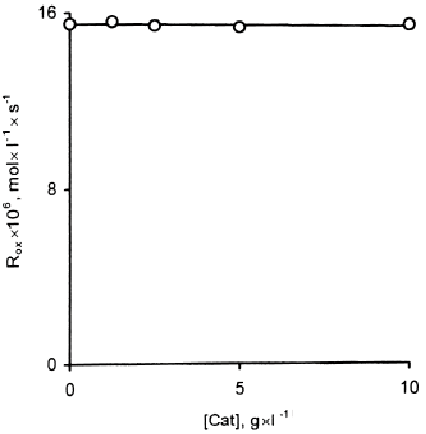


Figure 8. Dependence of initial rate of cyclooctene oxidation process on content of VSi_2 in the presence of AIBN. Reaction conditions: [Ol] = 4,1 mol L^{-1}; [AIBN] = 2×10^{-2} mol L^{-1}.

$$R_{ox} = \frac{-d[O_2]}{dt} = \frac{k_p}{\sqrt{k_t}}[Ol]\sqrt{R_i} = j\ [Ol]\sqrt{R_{fn} + R_{fc}} \qquad (4)$$

where $\varphi = \frac{k_p}{\sqrt{k_t}}$; R_i – rate of radicals formation; R_{fn} – rate of radicals formation by Reaction 1; R_{fc} – rate of radical formation by Reaction 2.

Considering the stage of radical formation reactions, applying steady state approximation [19] and assuming that $k_3 >> k_{-3}$, the rates of radical formation is described by the equations:

If to accept that the radical formation reactions are

$$R_{fn} = k_n[Z_1] = \frac{k_n k_1[TBHP]^2}{k_{-1} + k_n + k_2[Cat]}$$

$$R_{fc} = k_c[Z_2] = \frac{k_c k_1 k_2[TBHP]^2[Cat]}{(k_{-1} + k_n + k_2[Cat])(k_{-2} + k_c + k_3[Ol]^2)}$$

rate-limiting stages of the oxidation process, then:

$$k_{-1} + k_2[Cat] >> k_n \text{ and } k_{-2} + k_3[Ol]^2 >> k_c.$$

In this case:

$$R_{fn} = \frac{k_n k_1[TBHP]^2}{k_{-1} + k_2[Cat]} = \frac{k_n \frac{k_1}{k_{-1}}[TBHP]^2}{1 + \frac{k_2}{k_{-1}}[Cat]} = \frac{k_n K_1[TBHP]^2}{1 + \alpha[Cat]}$$

$$R_{fc} = \frac{k_c k_1 k_2[TBHP]^2[Cat]}{(k_{-1} + k_2[Cat])(k_{-2} + k_3[Ol]^2)} =$$

$$= \frac{k_c \frac{k_1}{k_{-1}}\frac{k_2}{k_{-2}}[TBHP]^2[Cat]}{\left(1 + \frac{k_2}{k_{-1}}[Cat]\right)\left(1 + \frac{k_3}{k_{-2}}[Ol]^2\right)} = \frac{\beta K_1[TBHP]^2[Cat]}{(1 + \alpha[Cat])(1 + \gamma[Ol]^2)}$$

where $\alpha = \frac{k_2}{k_{-1}}$; $\beta = k_c\frac{k_2}{k_{-2}}$; $\gamma = \frac{k_3}{k_{-2}}$; $K_1 = \frac{k_1}{k_{-1}}$.

Substituting the equations for R_{fh} and R_{fc} into the Eq. 4, we obtain the following equation of the rate of cyclooctene oxidation by molecular oxygen in the presence of both VSi_2 and TBHP in the reaction system:

$$R_{ox} = \varphi[Ol][TBHP]\sqrt{\frac{\beta K_1}{\alpha(1 + \gamma[Ol]^2)}} \qquad (5)$$

In the area where the reaction rate slightly depends on catalyst content, (at catalyst content higher than 5 g L^{-1}) Eq. 5 can be written as:

$$R_{ox} = \varphi[Ol][TBHP]\sqrt{\frac{K_1(k_n + \beta[Cat] + \gamma k_n[Ol]^2)}{(1 + \alpha[Cat])(1 + \gamma[Ol]^2)}}$$

This equation can be expressed in the next linear form for the dependence of the reaction rate on olefin concentration:

$$\frac{(\varphi[TBHP])^2}{R_{ox}^2} = \frac{\alpha \cdot \gamma}{\beta K_1} + \frac{\alpha}{\beta K_1} \times \frac{1}{[Ol]^2}$$

As seen from Fig. 9 this dependence, where

$$L = \frac{(\varphi[TBHP])^2}{R_{ox}^2}$$

is indeed observed. The value γ, and correspondingly the constants ratio k_3/k_{-2}, was found from the ratio of *Y*-axis intercept of the line (Fig. 9) to tangent of line inclination. This value is equal 0.22 L mol^{-1}.

With the purpose to find the values of other constants the Eq. 5 can be written as:

$$M = \frac{R_{ox}^2(1 + \alpha[Cat])}{(\varphi[Ol][TBHP])^2} = k_n K_1 + \frac{\beta K_1}{1 + \gamma[Ol]^2}[Cat]$$

The value of α in the expression for M is unknown. That is why to find the α we have substituted in the expression for M such value of α in the case of which the correlation coefficient of linear dependence in coordinates M on [Cat] was maximal (Fig. 10). The optimal value of α, and correspondingly the constants ratio k_2/k_{-1}, was found to be 0.45 L g^{-1} at correlation coefficient 0.99.

From the *Y*-axis intercept of the line and the tangent of line inclination of the dependence in Fig. 10 using the previously found value of γ as well as values of $K_1 = 0.8$ L mol^{-1} and $\varphi = 2.1\times10^{-3}$ $L^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$ presented in [20,21], respectively, the constants $k_n = 7.5\times10^{-5}$ s^{-1} and $\beta = 2.5\times10^{-3}$ L g^{-1} s^{-1} were estimated.

For confirmation the assumptions about the processes proceeding in the investigated reaction systems on initial stages of the oxidation process, from the Eq. 5 with the use of determined by us rate constants the theoretical dependences of the initial oxidation rate on catalyst content as well as concentrations of TBHP and cyclooctene were calculated and compared with the same obtained by experimental way. As it can be seen from Figs. 2, 6 and 7 the theoretically calculated R_{ox} values are in excellent agreement with the experimental data. It illustrates the correctness of our assumptions.

In order to get insight into the complex formation processes, which takes place on the catalyst surface, IR spectra (Fig. 11) of vanadium disilicide after interaction with the reaction mixture (1), cyclooctene (2) and TBHP (3) as well as the spectrum of initial VSi_2 (4) were recorded.

One can see that the spectrum of initial vanadium disilicide (4) has absorption peaks near 802, 1055, 1101, 1631 and 3434 cm^{-1}. The absorption bands at

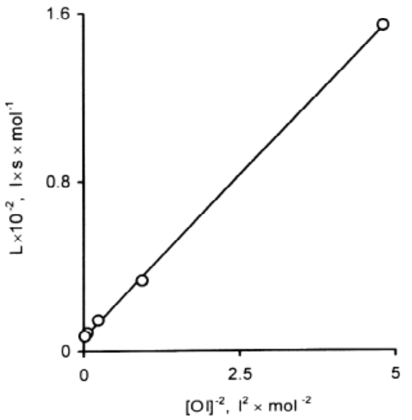


Figure 9. Dependences of L on $[Ol]^{-2}$.

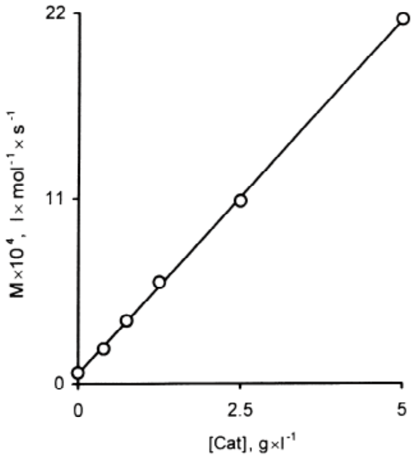


Figure 10. Dependences of M on content of VSi_2.

802 and 1101 cm^{-1} can be attributed to symmetric and asymmetric stretching of the Si-O vibrations [10], and 1055 to absorption of V=O [22] group. The broad absorption band at around 1631 is due to the bending mode vibration of water molecules and at around 3434 cm^{-1} is due to stretch mode vibration of –OH bonds [23-25].

After interaction with the reaction mixture, cyclooctene and TBHP in IR spectra 1-3 (Fig. 11) compare with spectrum 4 of initial VSi_2 the absorption peak in the range of 1178-1182 cm^{-1} is appeared. The band in the range of 1166-1180 cm^{-1} in spectra 1-3 indicates the presence of the C–O group on the catalyst surface, which is formed as a result of the interaction of TBHP and cyclooctene with surface of vanadium disilicide [26,27].

The absorption band of the C–O group in spectra 1-3 has practically the same value (1182 and 1178 cm^{-1}). According to this fact, one may conclude that the same catalytic center of VSi_2 forms the complex with both TBHP and cyclooctene. Therefore, TBHP can be replaced by cyclooctene in the catalytic active complex Z_2 of radical formation when the cyclooctene concentration increases. Consequently, the rate of radical formation as a result of catalytic decomposition of TBHP is decreased as it was observed experimentally.

Summarizing the experimental results obtained by us and the literature data [3,28], in Fig. 12, we propose the general kinetic model of the initial stages of cyclooctene oxidation with molecular oxygen in the presence of *tert*-butyl hydroperoxide, catalyzed by VSi_2.

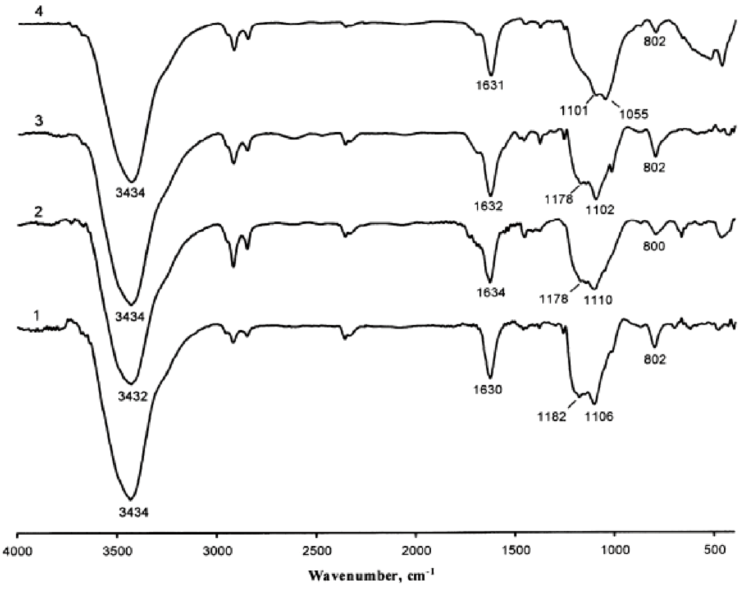


Figure 11. IR spectra of VSi_2 after interaction with reaction mixture (1), cyclooctene (2) and TBHP (3) as well as spectrum of initial VSi_2 (4).

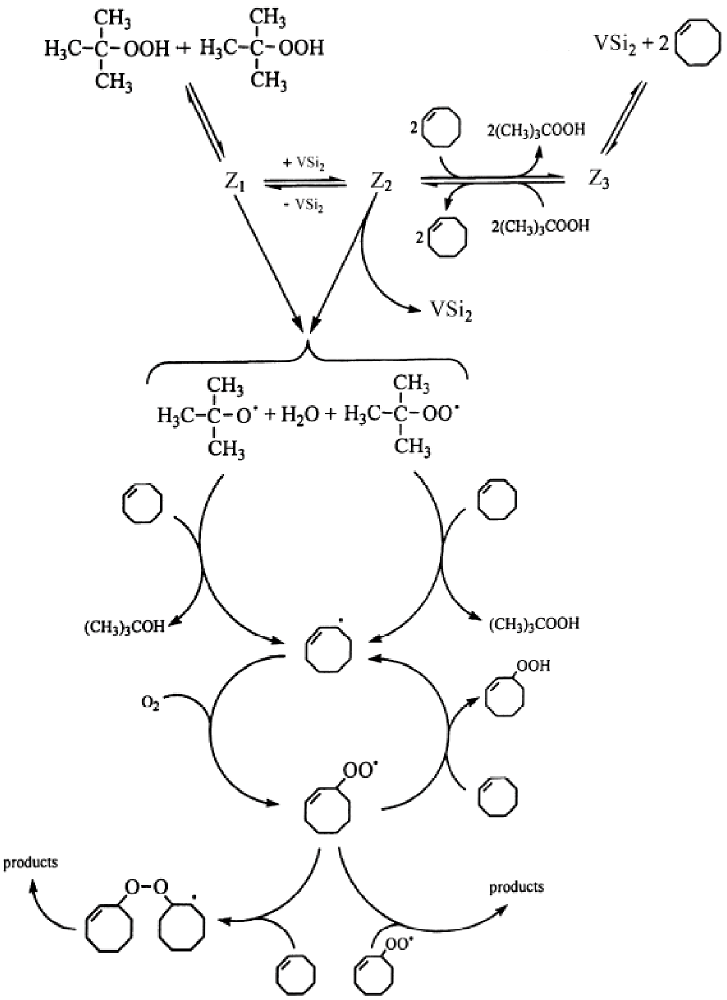


Figure 12. The kinetic model of the initial stages of cyclooctene oxidation with molecular oxygen in the presence of tert-butyl hydroperoxide catalyzed by VSi$_2$.

4. Conclusions

Thus, the obtained results indicate that catalytic effect of VSi$_2$ on initial stages of the oxidation process of cyclooctene by molecular oxygen is observed only in the presence of hydroperoxide in the reaction system. The activating role of vanadium disilicide deals with participation in the radical formation reaction. In the investigated system the formation of radicals is the result of two parallel processes – the process of noncatalytic and catalytic decomposition of hydroperoxide. The reaction is first order with respect to hydroperoxide and less than first order with respect to cyclooctene and catalyst.

The catalyst was characterized by FTIR before and after oxidation reaction. FTIR investigation has shown that hydroperoxide as well as cyclooctene are complexing with the same catalytic center of VSi$_2$.

The kinetic scheme of the investigated process was proposed from the obtained data. The equation for the reaction rate from the scheme was derived. All dependences of reaction rate on the concentration of reactants and catalyst content were described by this equation.

Further investigations will be focused on studies of the regularities of the oxidation process of olefins by molecular oxygen in the presence of other metal disilicides as well as on studies of deep stages of the cyclooctene oxidation process.

Acknowledgements

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