ISSN 1070-4272, Russian Journal of Applied Chemistry, 2008, Vol. 81, No. 9, pp. 1568–1572. © Pleiades Publishing, Ltd., 2008.
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## ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

# Kinetics of Oxidation of Methane to Formaldehyde on $Na_4[PFeMo_{11}O_{40}]/SiO_2$

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Received November 26, 2007

**Abstract**—The kinetics of oxidation of $CH_4$ to formaldehyde on the catalytic system $Na_4[PFeMo_{11}O_{40}]/SiO_2$ were studied, and a significant role of the redox potential of the $CH_4$–$O_2$ system with respect to the catalyst was shown. The density of centers participating in the reaction was determined, and dissociative competitive adsorption of methane and oxygen was established. The equation was deduced in the framework of the Langmuir–Hinshelwood theory taking into account the side conversion of formaldehyde. Possible participation of lattice oxygen in the reaction was suggested.

**DOI:** 10.1134/S1070427208090188

It was shown previously [1, 2] that, in oxidation of methane-containing gases with atmospheric oxygen in the presence of heteropoly compounds of the 12th series containing two ambivalent metals, it is possible to increase the conversion of methane by a factor of 2, the yield of formaldehyde by a factor of 3, and the catalyst performance by a factor of 40 in comparison with the known results.

Proceeding with studies on partial oxidation of methane, we examined the kinetics and mechanism of reaction on the $Na_4[PFeMo_{11}O_{40}]/SiO_2$ catalyst.

Oxidation was performed at 650°C in a batch reactor operating under conditions of quasiequilibrium kinetics when the methane conversion in single pass did not exceed 0.1%. In practice. the chosen operation mode means that the reactor operates under conditions of pseudozero conversion of methane. To avoid any kinetic restrictions that could be imposed by a high conversion of oxygen, we took into account the degree of methane conversion at oxygen conversion less than 20%.

The data obtained (Table 1) allow us to make the following conclusions: (1) An increase in the partial pressure of the reactants results in an increase in the reaction rate; however, the effect of methane pressure $P_{CH_4}$ is stronger; (2) variation of $P_{CH_4}/P_{O_2}$ does not significantly affect the selectivity of formaldehyde formation (71–77%), which depends in this case on formation of by-products, CO and $CO_2$ [3].

It is well known [4] that the activity of the catalysts for partial oxidation of methane is directly related to their ability to stabilize the reduced surface centers, which act as oxygen promoters in the redox cycle under the conditions of a dynamic equilibrium.

To estimate the dynamic equilibrium at the catalyst surface, we studied oxygen uptake by the surface at 650°C by the procedure described in [5] (Table 2). To analyze the data, let us introduce several designations for the catalyst surface: $\mu$ (nmol g$^{-1}$), number of physically reduced centers; $\mu_0$ (nmol g$^{-1}$), total number of centers capable of reduction; and $\theta_{red}$, density (fraction) of reduced centers at the surface.

Our data show that the absolute values of the partial pressure of the reactants do not affect $\mu$, but this quantity is affected by the ratio of these parameters. For example, the number of physically reduced centers varies from 15 to 65 for $P_{CH_4}/P_{O_2}$ ratios equal to 0.5 and 8.0, respectively, whereas in the absence of oxygen $\mu_0$ is equal to 350 nmol g$^{-1}$.

To elucidate the influence of reactants on reduction of the catalyst centers, we constructed a logarithmic dependence $\ln\theta_{red} = f(\ln P)$ (Fig. 1) on the basis of data presented in Table 2.

The slopes of the curves having opposite trends show that the reaction order with respect to oxygen and methane is close to 0.5, with the order with respect to oxygen being negative. These dependences

**Table 1.** Influence of the partial pressure of the reactants on the rate and selectivity of formaldehyde formation in oxidation of methane on $Na_4[PFeMo_{11}O_{40}]/SiO_2$ at 650°C

| Partial pressure, atm | | $P_{CH_4}/P_{O_2}$ | Conversion of $CH_4$/μ, % | $r_{CH_4}$, mol $s^{-1}$ $g^{-1}$ | Selectivity with respect to products, % | | |
|---|---|---|---|---|---|---|---|
| methane | oxygen | | | | $CH_2O$ | CO | $CO_2$ |
| 0.09 | 0.18 | 0.5 | 4.5 | 1.0 | 75 | 19 | 6 |
| 0.17 | 0.18 | 1.0 | 4.3 | 1.9 | 76 | 16 | 8 |
| 0.35 | 0.18 | 2.0 | 3.5 | 3.3 | 77 | 18 | 5 |
| 0.70 | 0.18 | 4.0 | 3.4 | 6.4 | 74 | 20 | 6 |
| 1.04 | 0.18 | 6.0 | 3.7 | 10.0 | 71 | 20 | 9 |
| 1.35 | 0.18 | 7.5 | 3.2 | 11.0 | 71 | 23 | 6 |
| 0.41 | 0.05 | 8.0 | 2.9 | 2.8 | 73 | 22 | 5 |
| 0.40 | 0.02 | 20.0 | 2.1 | 2.1 | 75 | 20 | 5 |

indicate that the redox potential of the $CH_4$–$O_2$ system relative to the catalyst plays a significant role. In other words, both reactants interact with the contact surface by the redox mechanism, and the influence of the partial pressure of the reactants on the reaction rate is caused by inhibition of desorption. It is evident that the dynamic equilibrium at the catalyst surface is reached in the point of intersection of the pressure dependences of the reduced center concentration and corresponds to $\ln P = -2$ (Fig. 1).

Thus, half-order dependence of $\theta_{red}$ on $P_{CH_4}/P_{O_2}$ evidently suggests the dissociative competitive activation of methane and oxygen molecules at the surface centers of the catalyst, and its algebraic form is as follows: $\theta_{red} = (P_{CH_4}/P_{O_2})^{0.5}$ This means that two active centers can participate in chemisorption of each reactant.

In the latter case, at inhibited desorption, the following reactions can occur at the catalyst surface:

$$CH_4 + 2\mu_1 \rightarrow CH_2O + 2\mu_2, \qquad (1)$$

$$O_2 + 2\mu_2 \rightarrow 2\mu_1, \qquad (2)$$

where $\mu_1$ is the number of oxidized centers and $\mu_2$ is the number of reduced centers.

Under the conditions of dynamic equilibrium,

$$[\mu_1] + [\mu_2] = [\mu_0]. \qquad (3)$$

Then, the rate of formation of reduced centers $r_{red}$ can be written in the form

**Table 2.** Influence of the partial pressure of reactants on absolute μ and fractional $\theta_{red}$ densities of reduced centers on the catalyst surface

| $P_{CH_4}/P_{O_2}$ | $P_{CH_4}$ | $P_{O_2}$ | μ, nmol $g^{-1}$ | $\theta_{red} \times 10^2$ |
|---|---|---|---|---|
| | atm | | | |
| 0.5 | 0.05 | 0.10 | 15 | 4 |
| 0.5 | 0.20 | 0.40 | 15 | 4 |
| 1.0 | 0.10 | 0.10 | 23 | 6 |
| 1.0 | 0.20 | 0.20 | 23 | 6 |
| 2.0 | 0.20 | 0.10 | 30 | 8 |
| 2.0 | 0.40 | 0.20 | 30 | 8 |
| 4.0 | 0.10 | 0.05 | 47 | 12 |
| 4.0 | 0.40 | 0.10 | 43 | 12 |
| 8.0 | 0.20 | 0.05 | 65 | 17 |
| 8.0 | 0.80 | 0.1 | 65 | 17 |
| – | 0.05 | – | 350 | 100 |

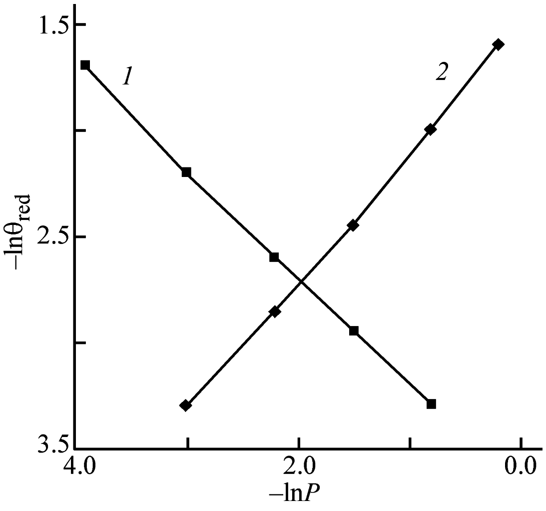

**Fig. 1.** Density of centers reduced at the surface $\theta_{red}$ as a function of (*1*) air and (*2*) methane pressure (log–log plots).

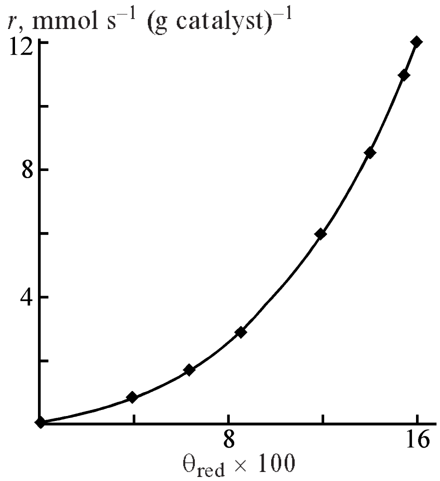

**Fig. 2.** Rate of methane oxidation $r$ as a function of the fraction of centers reduced at the surface $\theta_{\text{red}}$.

$$r_{\text{red}} = k_{\text{red}}P_{\text{CH}_4}(\mu_0 - \mu)^2. \qquad (4)$$

It is well known [6] that the rate of surface diffusion of lattice oxygen ions in the $\text{SiO}_2$ support is negligible under the conditions of methane oxidation; however, the rate of their diffusion in phosphorus–iron–molybdenum catalyst is unknown. Based on some indirect data, it can be assumed that the catalyst fragment Mo=O donates its oxygen atom to the methyl radical to form surface methoxyl transforming into formaldehyde and methanol at elevated temperatures. At least, iron–molybdenum catalyst for oxidation of methanol into formaldehyde operates in such a way [7]. The released lattice oxygen is compensated by oxygen from the medium. However, at such a low conversion of methane (below 5%), the possible role of lattice oxygen cannot be neglected in deducing the rate equation. At the same time, the oxygen source cannot affect the rate equation since the inner balance with respect to oxygen is kept due to the compensating mechanism of its transformation. Then we assume that, under dynamic equilibrium, the rate of disappearance of reduced centers practically coincides with the rate of catalyst oxidation $r_{\text{ox}}$:

$$r_{\text{ox}} = k_{\text{ox}}P_{\text{O}_2}\mu^2. \qquad (5)$$

Taking into account that $\theta_{\text{red}} = \mu/\mu_0$ and $\theta_{\text{red}}$ is limited by the condition $0 < \theta_{\text{red}} < 1$, the rates of reduction and oxidation of centers under dynamic equilibrium can be expressed as

$$k_{\text{ox}}P_{\text{O}_2}\mu^2\theta_{\text{red}} = k_{\text{red}}P_{\text{CH}_4}\mu_0^2(1 - \theta_{\text{red}})^2. \qquad (6)$$

Solving Eq. (6) relative to $\theta_{\text{red}}$, we obtain the following equation for the fraction (density) of reduced centers:

$$\theta_{\text{red}} = \frac{(k_{\text{ox}}/k_{\text{red}})^{0.5}(P_{\text{CH}_4}/P_{\text{O}_2})^{0.5}}{1 + (k_{\text{ox}}/k_{\text{red}})^{0.5}(P_{\text{CH}_4}/P_{\text{O}_2})^{0.5}}. \qquad (7)$$

This expression corresponds to the experimental dependence $\theta_{\text{red}} = (P_{\text{CH}_4}/P_{\text{O}_2})^{0.5}$ under the condition that $k_{\text{red}}P_{\text{CH}_4}/k_{\text{ox}}P_{\text{O}_2} \ll 1$.

Treatment of data listed in Table 2 by the nonlinear regression analysis using Eq. (7) allowed estimation of $k_{\text{red}}/k_{\text{ox}}$ at $4.5 \times 10^{-3}$. The value obtained suggests that the rate of catalyst oxidation is significantly higher than the rate of its reduction.

Since reactions (1) and (2) are irreversible, the rate of methane conversion $r_{\text{CH}_4}$ under dynamic equilibrium should be equal to the rate of these two stages: $r_{\text{CH}_4} = r_{\text{ox}} = r_{\text{red}}$. Then, the oxidation rate can be expressed through Eqs. (4) and (5):

$$r_{\text{CH}_4} = k_{\text{ox}}P_{\text{O}_2}\mu_0^2\theta_{\text{red}}^2 = k_{\text{red}}P_{\text{CH}_4}\mu_0^2(1 - \theta_{\text{red}})^2. \qquad (8)$$

The resulting dependence of the rate of methane oxidation is mathematically identical to the expression for second-order equation where one of the functions is $\theta_{\text{red}}$. Indeed, this conclusion is confirmed by the experimental dependence shown in Fig. 2.

Substituting $\theta_{\text{red}}$ from Eq. (7) into Eq. (8) and solving these equations with respect to the oxidation rate, we obtain the following expression:

$$r_{\text{CH}_4} = \mu_0^2\frac{k_{\text{red}}P_{\text{CH}_4}}{[1 + (k_{\text{red}}P_{\text{CH}_4}/k_{\text{ox}}P_{\text{O}_2})^{0.5}]^2}. \qquad (9)$$

Analyzing expression (9) from the mathematical standpoint, we can note that, at the ratio $P_{\text{CH}_4}/P_{\text{O}_2} \to \infty$, the model predicts zero reaction rate. Further, from the equation it follows that the reaction order with respect to $P_{\text{CH}_4}$ is fractional, especially at high $P_{\text{CH}_4}/P_{\text{O}_2}$ ratios, since with increasing methane content the degree of reduction of the catalyst surface increases. This naturally results in decreasing concentration of oxidized centers responsible for activation of methane.

The reliability of the kinetic model was confirmed by comparing the experimental and theoretical data. Nonlinear regression analysis of the curve presented in Fig. 2 gives $k_{\mathrm{red}}$ and $k_{\mathrm{ox}}$ equal to $9 \times 10^7$ and $4.5 \times 10^{-3}$ mol s$^{-1}$ atm$^{-1}$; in this case, $k_{\mathrm{red}}/k_{\mathrm{ox}}$ is equal to $4.5 \times 10^{-3}$. Good agreement between the calculated and experimental data supports our kinetic model.

However, it is necessary to consider one more aspect of this problem, namely, oxygen consumption for secondary transformations of formaldehyde (to carbon oxide and carbon dioxide). According to published data [8], oxidation of CO to $CO_2$ proceeds at a significantly lower rate than conversion of formaldehyde to carbon oxide; therefore, we took into account one more reaction pathway:

$$CH_2O + \rho_1 \rightarrow CO + H_2O + \rho_2. \qquad (10)$$

In the total rate of oxygen consumption, we considered two pathways: major and secondary, which can be described mathematically in the following way:

$$r_{O_2} = r_{CH_4}(1 + S_{CO}\alpha), \qquad (11)$$

where $\alpha$ is the stoichiometric coefficient in reaction (10).

Continuing mathematical transformations and substitutions, we can obtain from Eq. (7) the following expression:

$$\theta_{\mathrm{red}} = \frac{[(1+n)(k_{\mathrm{ox}}/k_{\mathrm{red}})]^{0.5}(P_{CH_4}/P_{O_2})^{0.5}}{1 + [(1+n)(k_{\mathrm{ox}}/k_{\mathrm{red}})]^{0.5}(P_{CH_4}/P_{O_2})^{0.5}}, \qquad (12)$$

where $n = S_{CO}\alpha$.

Substituting complete expression for $\theta_{\mathrm{red}}$ (12) in Eq. (8), we obtain the following equation for rate of methane oxidation:

$$r_{CH_4} = \rho_2^0 \frac{k_{\mathrm{red}} P_{CH_4}}{\{1 + [(1+n)(k_{\mathrm{ox}}/k_{\mathrm{red}})]^{0.5}(P_{CH_4}/P_{O_2})^{0.5}\}^2}. \qquad (13)$$

This expression shows not only the dependence of the reaction rate on the partial pressures of reactants but also inverse dependence of the reaction selectivity: the larger the amount of CO formed, the deeper the reduction of the catalyst surface, which results in decreased rate of the main reaction. It should be noted that the very low $k_{\mathrm{red}}/k_{\mathrm{ox}}$ ratio in the examined range of $P_{CH_4}/P_{O_2}$ is not a significant factor, since higher value of $k_{\mathrm{ox}}$ does not noticeably affect the reaction rate due to pseudo-first order of the reaction rate with respect to methane. On the contrary, at high $P_{CH_4}/P_{O_2}$ ratios, the reaction rate should increase and its dependence on $P_{O_2}$ should be insignificant. In practice this means that the concentration of sorbed methane, rather than the concentration of the oxidizing agent, becomes important. This is quite logical since the rupture of the $CH_3$–H bond in chemisorption of methane is the limiting stage. In addition, in formation of $CH_3O$ the source of oxygen is presumably lattice oxygen.

Thus, it can be concluded that oxidation of methane to formaldehyde at the surface of $Na_4 \cdot [PFeMo_{11}O_{40}]/SiO_2$ catalyst proceeds by a concerted mechanism involving activation of gas-phase oxygen at the surface of reduced catalyst centers and subsequent its addition to activated molecule of methane. Compensation of lattice oxygen with molecular oxygen is equally probable, especially because this process on heteropoly compounds proceeds instantaneously [9]. The latter factor suggests that the role of lattice oxygen is more significant than it was believed previously. Since completion of the lattice with oxygen is not the activated stage of the process [10], experimental consideration of its role without using special methods is difficult. In this case, one could rely on the published data [11, 12] obtained using an isotopic label. Unfortunately, these results are ambiguous because they do not allow determination of the nature of the oxygen source. In addition, based on these data, we might prefer the version of "intercalation" of molecular oxygen. However, this conclusion is not well-founded, since the content of $^{18}O$ in the catalyst was not determined after the reaction completion.

The only confirmation of the participation of lattice oxygen in the process is the experiment in which oxygen-free methane was passed through a catalyst bed with increased content of acting base (up to 10%). Among reaction products, traces of formaldehyde were found and the reaction quickly ceased. However, after contact of the catalyst with atmospheric oxygen, the contact activity was restored and formaldehyde was found among the reaction products again.

These data suggest that oxidation of methane can proceed, at least partially, due to participation of lattice oxygen whose consumption is compensated by oxygen from the reaction medium.

## CONCLUSIONS

(1) In studying the kinetics of methane oxidation to formaldehyde, it was found that the redox poten-

tial of the $CH_4$–$O_2$ system relative to the catalyst plays a significant role, and the dissociative competitive adsorption of methane and oxygen was suggested.

(2) The reaction rate depends on the partial pressure of methane and is inversibly proportional to the reaction selectivity, due to deep reduction of the surface with carbon monoxide formed as by-product.

(3) The experimental data and especially the features of the behavior of all heteropoly compounds suggest that lattice oxygen of the heteropoly compound participates in the reaction; the vacancy formed is filled with oxygen of the reaction medium.

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