Kinetics of Petroleum Sulfides Peroxidation in the Presence of Two Catalysts

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Kinetics was studied and the scheme of the reaction of petroleum sulfides peroxidation to sulfoxides in the presence of catalytic systems «molybdic acid + molybdenum oxide (VI)» and «molybdic acid + wolframic acid» was proposed.

Key words: petroleum sulfides, sulfoxides, oxidation, hydrogen peroxide, molybdic and wolframic acids, molybdenum oxide, kinetic models

In the research works¹⁻⁹ we showed that kinetics and products of petroleum sulfides peroxidation to sulfoxides depends on the reactivity and mechanism of molybdic compounds catalytic effect. The present work is the continuation of this research and is devoted to the study of kinetics of petroleum sulfides peroxidation under the influence of hydrogen peroxide and mixtures of two catalysts «molybdic acid + molybdenum oxide (VI)» and «molybdic acid + wolframic acid».

Main part

Experimental technique. Sulfides of straight run diesel of Arlanskaya oil with the boiling temperature range from 180°C up to 360°C represented by derivative thiocyclopentanes, thiocyclohexanes, dialkyl- and phenylalkyl sulfides¹⁰ were oxidized in the reactor with the mechanical agitator in accordance with the technique described in the work¹¹. During this process was performed intermittent sampling for

sulfoxides analyses. Before performing the test, mixtures of catalysts composed of molybdic and wolframic acids and molybdenum oxide (VI) were kept in hydrogen peroxide for 30 minutes.

Analysis of sulfoxy sulfur in the diesel fuel oxidate was carried out by nonaqueous potentiometric titration with the chloric acid solution in dioxane¹².

Sulfoxy sulfur content S (% wt) is calculated by the following formula:

$$S = \frac{V \cdot N \cdot 32 \cdot 100}{P \cdot 1000} = \frac{3.2 \cdot V \cdot N}{P}$$

where, V – volume 0,05 mole/dm³ (0,05n) of chloric acid solution in dioxane, used for titration, cm^3 ;

N - molarity of chloric acid solution in dioxane; P- sample weighted quantity, g;

32- sulfur atomic weight.

Results discussing

When using MOO_3 and H_2MOO_4 catalysts, various kinetics could be observed in the reaction of petroleum sulfides peroxidation, although in both cases the oxidizer is peroxymolybdenum acid [1-

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3]. Although catalytic behavior of molybdic and wolframic acids in the reaction of petroleum sulfides peroxidation is the same, oxidizers in these systems are different peroxo-compounds (H_2MoO_5 and H_2WO_5). For further studying of the mechanism of catalytic petroleum sulfides peroxidation were used binary catalytic systems composed of catalysts that differ in reactivity and catalytic effect.

Sulfides peroxidation in the presence of H₂MoO₄ and MoO₃

When using combined catalytic systems $H_2MoO_4 + MoO_2$ conjugate character of petroleum sulfides peroxidation reaction (R₂S) could be observed. This could be proved by the kinetic curves of petroleum sulfoxides accumulation (R_2SO) . During the test with the individual MoO₃, rate of R₂SO accumulation at the initial stages increases and during the test with H₂MoO₄, rate of R_2 SO accumulation decreases (fig. 1). In the tests with combined catalytic system kinetic curves of petroleum sulfoxides accumulation could be considered as the combination of kinetic curves obtained during the tests with individual catalysts. The obtained results could be explained on the basis of the following scheme of petroleum sulfides oxidation under the influence of " $H_2O_2 + H_2MoO_4 +$ MoO₃" oxidation system.

 $H_2M_0O_4 \cdot H_2O_2 = (^{(1)}H_2M_0O_5 + H_2O$ (1.1)

$$MoO_3 + H_2O_2 - (2)H_2MoO_5$$
 (1.2)

 $^{(1)}H_2 M_0 O_5 + R_2 S \longrightarrow {}^{(1)}H_3 M_0 O_5 - R_2 S$ (2.1)

$$^{(2)}H_2M_0O_5 = R_2S = (^{2)}H_2M_0O_5 \cdots R_2S$$
 (2.2)

$${}^{(1)}H_2M_0O_5 - R_2S \longrightarrow {}^{(1)}H_2M_0O_4 - {}^{(1)}R_2SO$$
 (3.1)

$$^{(2)}H_2M_0O_5 - R_2S \longrightarrow ^{(2)}H_2M_0O_6 (2)R_2SO$$
 (3.2)

In this scheme sulfoxide is accumulated from two lines because the oxidizer – peroxymolybdenum acid is generated from two initial catalysts of the reactions (1.1) and (1.2). Total concentration of peroxymolybdenum acid is:

$$\begin{bmatrix} H_2 MoO_5 \end{bmatrix} = \begin{bmatrix} (^{(1)}H_2 MoO_5 \end{bmatrix} + \begin{bmatrix} (^{(2)}H_2 MoO_5 \end{bmatrix} = \\ = \begin{bmatrix} alpha \end{bmatrix} \begin{bmatrix} H_2 MoO_5 \end{bmatrix} + (1 - \begin{bmatrix} alpha \end{bmatrix}) \cdot \begin{bmatrix} H_2 MoO_5 \end{bmatrix}^{\dots(1)}$$

where [alpha] - mole fraction of peroxymolybdenum acid generated from H_2MoO_4 ; (1 - [alpha]) – mole fraction of peroxymolybdenum acid generated from MoO_3 ;

 α varies from 0 to 1.

Total rate of sulfides consumption in two lines amounts to

$$\mathbf{V} = \mathbf{V}_1 + \mathbf{V}_2 \qquad \dots (2)$$

On the basis of the principle of elementary steps independence we can obtain the equation for calculation of V_1 and V_2 .

Earlier in the work [1] it was mentioned that the process of sulfides peroxidation in the presence of molybdic acid is limited by the complex decomposition stage (3.1)

$$\mathbf{V}_1 = [alpha] \cdot \mathbf{k}_{3,1} \Big|^{(1)} \mathbf{H}_2 \mathbf{MoO}_5 \cdots \mathbf{R}_2 \mathbf{S} \Big| \dots (3)$$

Taking into account quasistationarity of complex concentration, equation (3) transforms as follows:

$$V_{1} = -\frac{d[R_{2}S]}{dt} = \frac{\alpha \cdot k_{2,1} \cdot k_{2,1}}{k_{2,1} + k_{-\alpha,1}} \left[{}^{(1)}H_{2}MoO_{2} \right] \cdot [R_{2}S] = \left[\alpha lp ka \right] {}^{(1)}k_{ab} \cdot [R_{2}S] \dots (4)$$

where

⁽¹⁾
$$\mathbf{k}_{s\dot{c}.} = \frac{\mathbf{k}_{3.1} \cdot \mathbf{k}_{2.1}}{\mathbf{k}_{3.1} + \mathbf{k}_{-2.1}} \cdot \left[{}^{(1)}\mathbf{H}_2\mathbf{MoO}_5 \right] \dots (5)$$

After separation of variables in the equation (4)

$$\frac{d[R_2S]}{[R_2S]} = [alpha]^{(1)}k_{so.} dt$$

Integration within the range from $[R_2S]_0$ to $[R_2S]_t$ and from 0 to t gives the equation of sulfides consumption kinetic curve.

$$\ln \frac{\left[\mathbf{R}_{2}\mathbf{S}\right]_{0}}{\left[\mathbf{R}_{2}\mathbf{S}\right]_{t}} = \left[alpha\right]^{(1)}\mathbf{k}_{s\dot{\omega}} \mathbf{t} \qquad \dots (6)$$

Maximum possible concentration of sulfoxides generated in this line comprises the certain amount from the initial sulfide concentration $[beta][R_2S]_0 = [{}^{(1)}R_2SO]_{e}$ or $[R_2S]_0 = [{}^{(1)}R_2SO]_{e}/[beta]$, and current sulfides concentration is connected with the current concentration of sulfoxides in the following way

$$[beta] [R_2S]_t = \begin{bmatrix} {}^{(1)}R_2SO \end{bmatrix}_m - \begin{bmatrix} {}^{(1)}R_2SO \end{bmatrix}_t$$

or

$$[\mathbf{R}_{2}\mathbf{S}]_{t} = (\lfloor^{(1)}\mathbf{R}_{2}\mathbf{S}\mathbf{O}\rfloor_{\infty} - \lfloor^{(1)}\mathbf{R}_{2}\mathbf{S}\mathbf{O}\rfloor_{t})/[\mathbf{beta}]$$

where β - amount of sulfoxides per

where β - amount of sulfoxides per consumed sulfide.

After substitution of these values into the equation (6) we obtain the equation of

sulfoxides accumulation kinetic curve.

 $ln([^{(1)}[R_2SO]]_{a} - [^{(1)}R_2SO]]_{a} - ln[^{(1)}R_2SO]]_{a} - [alpha]^{(1)}k_{ya} \cdot t...(7)$ Sulfides consumption in the second line

is probably also limited by the complex decomposition and is proceeds at the rate of

$$\mathbf{V}_{2} = \left(1 - [alpha]\right) \mathbf{k}_{3,2} \begin{bmatrix} a \\ B \end{bmatrix} \mathbf{H}_{2} \mathbf{M} \mathbf{o} \mathbf{O}_{5} \cdots \mathbf{R}_{2} \mathbf{S} \end{bmatrix} \qquad \dots (8)$$

Taking into account quasistationarity of complex concentration, equation (8) transforms as follows:

$$V_{z} = \frac{(1 - [alpha]) \cdot \mathbf{k}_{z,z} \cdot \mathbf{k}_{z,z}}{\mathbf{k}_{z,z} + \mathbf{k}_{z,z}} \cdot [{}^{(z)}\mathbf{H}_{z}\mathbf{MoO}_{z}] \cdot [\mathbf{R}_{z}\mathbf{S}] \qquad \dots (9)$$

It seems that equations (4) and (9) are similar but they are fundamentally different. The equation (4) includes balanced and practically constant concentration [$^{(1)}H_2MoO_5$], as it is formed and consumed in balanced stages (1.1) and (2.1) [1].

Peroxymolybdenum acid concentration in equation (9) will increase because ${}^{(2)}H_2MoO_5$ is generated in the irreversible stage (1.2). Rate of ${}^{(2)}H_2MoO_5$ accumulation equals to

$$\frac{d[^{(2)}H_2MoO_5]}{dt} = k_{1,2}[MoO_3] \cdot [H_2O_2] \dots (10)$$

Molybdenum oxide (VI) is used for testing in solid form, so its chemical potential is constant. So we can take $[MoO_3] = const$. Taking into account excess amount of hydrogen peroxide during testing, on the surface stages we can take $[H_2O_2] = const$. Then in equation (10) time and peroxoacid concentration are variable values.

In such case, from the equation

$$d[^{(2)}H_{2}MoO_{5}] = k_{1,2}[MoO_{3}] \cdot [H_{2}O_{2}]dt$$

After integration

$$\begin{bmatrix} (2) H_2 MoO_5 \end{bmatrix} = k_{12} \begin{bmatrix} MoO_3 \end{bmatrix} \cdot \begin{bmatrix} H_2 O_2 \end{bmatrix} \cdot t \dots (11)$$

After replacement of $[^{(2)}H_2MOO_5]$ in equation (9) taking into account equation (11) we have

$$\frac{d[R_2S]}{dt} = \frac{(1 - [alpha]) \cdot k_{2.2} \cdot k_{2.2} \cdot k_{1.2}}{k_{2.2} + k_{-2.2}} \cdot [R_2S] \cdot [MoO_2] \cdot [H_2O_2] \cdot t \dots (12)$$

If at the surface stages of the reaction we take $[R_2S] = const$, then

$$- d[R_{1}S] = \frac{(1-[aiphd]) \cdot k_{12} \cdot k_{12} \cdot k_{12}}{k_{12} + k_{22}} \cdot [R_{1}S] \cdot [MoQ] \cdot [H_{1}O_{1}] \cdot t \cdot dt = ...(13)$$

= (1-[aiphd])^{(2)}k_{12} \cdot t \cdot dt

where

⁽²⁾
$$\mathbf{k}_{sb.} = \frac{\mathbf{k}_{3.2} \cdot \mathbf{k}_{2.2} \cdot \mathbf{k}_{1.2}}{\mathbf{k}_{3.2} + \mathbf{k}_{-2.2}} \cdot [\mathbf{R}_2 \mathbf{S}] \cdot [\mathbf{MoO}_3] \cdot [\mathbf{H}_2 \mathbf{O}_2]$$

(14)

Integration from $[R_2S]_0$ to $[R_2S]_t$ and from 0 to t gives

$$-\Delta[\mathbf{R}_2\mathbf{S}] = \frac{1 - [alpha]}{2} \cdot {}^{(2)}\mathbf{k}_{\text{sec.}} \cdot \mathbf{t}^2 \dots (15)$$

where

$$-\Delta[\mathbb{R}_{*}\mathbb{S}] = -([\mathbb{R}_{*}\mathbb{S}]_{*} - [\mathbb{R}_{*}\mathbb{S}]_{*}) = \Delta[^{(2)}\mathbb{R}_{*}\mathbb{S}O] = [^{(2)}\mathbb{R}_{*}\mathbb{S}O]_{*} - [^{(2)}\mathbb{R}_{*}\mathbb{S}O]_{*} = [^{(2)}\mathbb{R}_{*}\mathbb{S}O]_{*}$$

because
$$\begin{bmatrix} {}^{(2)}\mathbf{R}_{2}\mathbf{SO} \end{bmatrix}_{0} = 0$$

Table 1. Values of effective constants of accumulation rate and amount ofsulfoxides when using $MoO_3 + H_2MoO_4 [R_2S]_{0=} 1,5 \%$ wt, $[H_2O_2] = 5,9 \%$ wt, $T = 60^{\circ}C$

Mole fractions of MoO ₃ /H ₂ MoO ₄ , %	100/0	60/40	50/50	40/60	0/100
	$2,1 \pm 0,3$ $1,00 \pm 0,25$ 43	$2,2 \pm 0,3$ $1,00 \pm 0,25$ 45	$2,3 \pm 0,3$ $1,01 \pm 0,25$ 47	$2,6 \pm 0,4$ $1,01 \pm 0,27$ 53	0,86 ± 0,18 92

Table 2. Values of the effective constants of accumulation rate and amounts of obtained sulfoxides when using mixtures $H_2MoO_4 + H_2WO_4 [R_2S]_{0=} 0.56 \%$ wt, $[H_2O_2] = 2.2 \%$ wt, $T = 60 \degree C$

Mole fractions of MoO ₃ /H ₂ MoO ₄ , %	100/0	90/10	70/30	30/70	10/90	0/100
	8,6 ± 1,8	$8,1 \pm 2,0$	$6,9 \pm 1,9$	$4,3 \pm 0,4$	$2,5 \pm 0,4$	$2,2 \pm 0,4$
	8,6	8,0	6,7	4,1	2,8	2,2
	92	89	81	54	52	45

then
$$\begin{bmatrix} {}^{(2)}\mathbf{R}_2\mathbf{SO} \end{bmatrix} = \frac{1 - [alpha]}{2} \cdot {}^{(2)}\mathbf{k}_{ab} \cdot \mathbf{t}^2 \dots (16)$$

Initial sections of kinetic curves of sulfoxides accumulation in the tests with MoO_3 (fig.1) become linear with the correlation coefficient 0,993 \div 0,995 within the coordinates of equation (16), where by the slope ratio were calculated the values of effective constants ⁽²⁾k_{MD} (table 1).

Kinetic curves of sulfoxides accumulation in the developed sulfides oxidation (fig. 1) are linear within the coordinates of equation (7) with the correlation coefficient $0,982 \div 0,987$. By the slope ratio of these transformations were calculated the values of effective constants of the rate ${}^{(1)}k_{MD}$ (table 1). Constance of ${}^{(1)}k_{MD}$ while varying of catalysts mixture compound (table 1), equation (5)) shows that in the developed oxidation in all tests there is the same balanced concentration of peroxymolybdenum acid, which represents the sum of $[^{(1)}H_2MoO_5]$ and $[^{(2)}H_2MoO_5]$ (equation (1)). This sum in all tests was the same as the initial concentrations of H₂MoO₄ and MoO₂ were taken in such ratio that the total amount of the substance (in moles) in conversion to metallic Mo were always the same.

Addition of H_2MoO_4 to MoO_3 increases the amount of the desired product but the amount of obtained R_2SO is not very high (table 1). It is obvious that usage of MoO_3 or $MoO_3 + H_2MoO_4$ mixture as the catalyst causes many side reactions



Fig.1. Kinetic curves of sulfoxides accumulation during sulfides oxidation with the combined catalytic system $H_2MOO_4 + MOO_3$. $[R_2S]_0 = 1,5 \%$ wt. $[H_2O_2]_0 = 5,9 \%$ wt. $T=60^{0}$ C. Fraction of H_2MOO_4 ,

%: 1 - 100, 2 - 60, 3 - 50, 4 - 40, 5 - 0

and the amount of the obtained desired product under condition of constancy of effective rate constants is low (table 1).

Sulfides peroxidation in the presence of H_2MoO_4 and H_2WO_4

Similar kinetics of sulfoxides accumulation during petroleum sulfides oxidation could be observed not only when using individual catalysts H_2MoO_4 or H_2WO_4 , but also when using combined catalytic system $H_2MoO_4 + H_2WO_4$ (fig. 2)

Data contained in figure 2 could be explained by the following scheme

$$H_2M_0O_4$$
, $H_2O_2 = H_2M_0O_5$, H_2O (41)

 $H_2WO_4 - H_2O_2 = H_2WO_5 - H_2O$ (4.2)

$$H_2M_2O_5 = R_2S \longrightarrow H_2M_2O_5 \cdots R_2S$$
 (5.1)

$$H_2WO_5 = R_2S \longrightarrow H_2WO_5 = R_2S$$
 (5.2)

$$H_2MoO_5 - R_2S \longrightarrow H_2MoO_4 (1)R_2SO$$
 (61)

$$H_2WO_5 - R_2S - H_3WO_4 = (2)R_2SO$$
 (6.2)

The proposed scheme consists of two catalytic cycles of sulfoxides generation, where sulfides oxidizers are H_2MoO_5 and H_2WO_5 correspondingly. Limiting stages are (6.1) and (6.2) of peroxoacids decomposition with the initial sulfide. So the total rate of sulfides consumption amounts to



Fig. 2. Kinetic curves of sulfoxides accumulation during sulfides oxidation with the combined catalytic system $H_2MoO_4 + H_2WO_4 [R_2S]_{0=} 0.56 \%$ wt, $[H_2O_2] = 2,2 \%$ wt, T = 60 °C. Fraction of $H_2MoO_4 \%$: $1 - 100, 2 - 90, 3 - 70, 4 - 30, 5 - 10, 6 - 0 (100\% H_2WO_4)$

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where [alpha] - mole fraction of H_2MoO_4 in the catalytic mixture (in conversion to metallic Mo);

 $(1 - [alpha]) - mole fraction of H_2WO_4$ in the catalytic mixture (in conversion to metallic W).

After application of the principle of quasistationarity for concentrations of peroxoacids complexes with the sulfide, the equation (17) transforms as follows

$$\begin{split} & -\frac{d[R_{+}S]}{dt} - \left(\frac{[alpha] \cdot k_{a,1} \cdot k_{a,2}}{k_{a,1} + k_{a,2}} \cdot [H_{a}MoC_{1}] + \frac{(1 - [alpha]) \cdot k_{a,2} \cdot k_{a,2}}{k_{a,2} + k_{a,2}} \cdot [H_{a}WC_{1}] \right) \cdot [R_{+}S] \\ & - ([alpha]^{1/2} k_{+6} + (1 - [alpha])^{1/4} k_{+6}) \cdot [R_{+}S] \\ (18) \\ & \text{where} \end{split}$$

$${}^{(3)}\mathbf{k}_{s\dot{\varpi}.} = \frac{\mathbf{k}_{6.1} \cdot \mathbf{k}_{5.1}}{\mathbf{k}_{6.1} + \mathbf{k}_{-5.1}} \cdot \left[\mathbf{H}_2 \mathbf{MoO}_5\right] \dots (19)$$

$${}^{(4)}\mathbf{k}_{s\dot{\varpi}.} = \frac{\mathbf{k}_{6.2} \cdot \mathbf{k}_{5.2}}{\mathbf{k}_{6.2} + \mathbf{k}_{-5.2}} \cdot \left[\mathbf{H}_2 \mathbf{WO}_5\right] \dots (20)$$

Correlations of (19) and (20) are lawful because they contain quasibalanced and practically constant concentrations of peroxoacids which are generated at the balanced stages. After integration of (18) within the range from $[R_2S]_0$ to $[R_2S]_1$ and from 0 to t we obtain the equation of sulfides consumption kinetic curve.

$$\ln \frac{[\mathbf{R}_{1}\mathbf{S}]_{a}}{[\mathbf{R}_{2}\mathbf{S}]_{a}} = ([\mathbf{alpha}]^{(2)}\mathbf{k}_{ab} + (1-[\mathbf{alpha}])^{(4)}\mathbf{k}_{ab})\mathbf{t} \dots (21)$$

Taking $\mathbf{S}[\mathbf{R}_{2}\mathbf{S}]_{a} = [\mathbf{R}_{2}\mathbf{S}\mathbf{S}]_{a}$

$$\mathbb{B}[\mathbb{R},\mathbb{S}] = [\mathbb{R},\mathbb{S}0]_{\mathbb{R}} - [\mathbb{R},\mathbb{S}0]_{\mathbb{R}}$$
, (where [beta] – amount of sulfoxides per consumed sulfide), and

$$[alpha]^{(6)}k_{ab} + (1-[alpha])^{(4)}k_{ab} = {}^{(atom-)}k_{ab} \dots (22)$$

We comprises the equation of sulfoxides

We comprises the equation of sulfoxides accumulation kinetic curve

$$\begin{split} \ln[\mathbb{R}_2 \mathbb{SO}]_{e} &- [\mathbb{R}_2 \mathbb{SO}]_{e} = \ln[\mathbb{R}_2 \mathbb{SO}]_{e} - \stackrel{(\text{arcc.})}{\longrightarrow} k_{\text{sc.}} \cdot t \dots (23) \\ \text{where } [\mathbb{R}_2 \mathbb{SO}]_{e} = \left[\stackrel{(1)}{\longrightarrow} \mathbb{R}_2 \mathbb{SO} \right]_{e} + \left[\stackrel{(2)}{\longrightarrow} \mathbb{R}_2 \mathbb{SO} \right]_{e}; \end{split}$$

Kinetic curves, contained in figure 2, are transformed with the correlation coefficient 0, 980 \div 0,995 into the direct lines from where were calculated the testing values of the effective

constant of the rate ${}^{(M:A?)}k_{MD}$ (table 2)

Calculation of the effective constant of the rate of sulfoxides accumulation ${}^{(@0AG)}k_{MD}$ using the equation (22) and taking into account mole fraction and values ${}^{(3)}k_{MD}$ and ${}^{(4)}k_{MD}$ of catalysts showed that testing and calculated values of the effective constant of the rate are practically the same, within the permitted experimental error (table 2). This means that when using combined catalytic system $H_2MOO_4 + H_2WO_4$ in the reaction of sulfides peroxidation two catalytic cycles are realized parallel and independently from each other.

Increasing of the fraction of less active wolframic acid in the mixture $H_2MoO_4 + H_2WO_4$ reduces the amount of obtained sulfoxides (table 2), obviously in the result of hydrogen peroxide decomposition in the side reactions.

CONCLUSION

Kinetics of sulfoxides accumulation during petroleum sulfides oxidation under the influence of oxidizing systems $H_2O_2 + H_2MoO_4 + MoO_3$ and $(H_2O_2 + H_2MoO_4 + H_2WO_4)$ depends on:

- a) On the kinetics of oxidizers accumulation peroxoacids;
- b) On the oxidation capacity of peroxoacids;
- c) On the number of side reactions of hydrogen peroxide decomposition.

Credits

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