

Appendix 1

In the framework of the dissociative adsorption model, the basic kinetic equations of the oxygen isotope redistribution in the “gas–solid state” system (6) are as follows:

$$\begin{aligned}\dot{\alpha} &= \rho_a(\alpha_a - \alpha) + \rho_{as}\left(\frac{1}{2}\alpha_a + \frac{1}{2}\alpha_s - \alpha\right) + \rho_s(\alpha_s - \alpha) \\ \dot{Z} &= \rho_a(\alpha_a^2 - C_{36}) + \rho_{as}(\alpha_a\alpha_s - C_{36}) + \rho_s(\alpha_s^2 - C_{36}) - 2\alpha\dot{\alpha}\end{aligned}\quad (\text{A1-1})$$

where α_a – ^{18}O oxygen isotope fraction in the adsorption layer.

Under adsorption–desorption equilibrium conditions, it is necessary to write down the isotope quasi-stationary (IQS) condition for all the “intermediate” particles.¹ In the framework of the dissociative adsorption model, the “intermediate” particle is the oxygen adatom, $(\text{O})_a$. The IQS condition corresponds to the equality to zero for the sum of all the incoming and outgoing mass flows regard to the graph vertex of atoms transfer for the oxygen adatom:²

$$(\rho_a + \rho_{as})(\alpha_a - \alpha) = \rho_i(\alpha_s - \alpha_a) \quad (\text{A1-2})$$

The IQS condition is an analogue of Kirchhoff's rules in the electrical circuit theory where the algebraic sum of electrical currents is equal to zero for any junction of the electrical circuit. Using (A1-2), we obtain the ^{18}O oxygen isotope fraction, α_a , for the adatoms as follows:

$$\begin{aligned}\alpha_a &= \alpha + p(\alpha_s - \alpha) \\ p &= \frac{\rho_i}{\rho_a + \rho_{as} + \rho_i} = \frac{\alpha_a - \alpha}{\alpha_s - \alpha}\end{aligned}\quad (\text{A1-3})$$

where p – possibility of incorporation.

Taking into account (A1-3) for (A1-1), we get the following:

$$\begin{aligned}\dot{\alpha} &= (\rho_a p + \frac{1}{2}\rho_{as}(p+1) + \rho_s)(\alpha_s - \alpha) \\ \dot{Z} &= -(\rho_a + \rho_{as} + \rho_s)Z + (\rho_a p^2 + \rho_{as}p + \rho_s)(\alpha_s - \alpha)^2\end{aligned}\quad (\text{A1-4})$$

¹V. S. Muzykantov, *React. Kinet. Catal. Lett.*, 1980, **14**(3), 311–316.

²V. S. Muzykantov, *React. Kinet. Catal. Lett.*, 1980, **13**(4), 419–424.

Appendix 2

In the framework of the two-step model A, the basic kinetic equations of the oxygen isotope redistribution in the “gas–solid state” system (6) are as follows:

$$\begin{aligned}\dot{\alpha} &= \rho_a(\alpha_a - \alpha) \\ \dot{Z} &= \rho_a(\alpha_a^2 - C_{36}) - 2\alpha\dot{\alpha}\end{aligned}\tag{A2-1}$$

Since in the framework of the two-step model A the “intermediate” particle is the oxygen adatom, $(O)_a$, the IQS condition is the following:

$$\rho_a(\alpha_a - \alpha) = \rho_i(\alpha_s - \alpha_a)\tag{A2-2}$$

Using (A2-2), we obtain the ^{18}O oxygen isotope fraction, α_a , for adatoms as the following:

$$\begin{aligned}\alpha_a &= \alpha + p(\alpha_s - \alpha) \\ p &= \frac{\rho_i}{\rho_a + \rho_i} = \frac{\alpha_a - \alpha}{\alpha_s - \alpha}\end{aligned}\tag{A2-3}$$

Taking into account (A2-3) for (A2-1), we get the following:

$$\begin{aligned}\dot{\alpha} &= \rho_a p(\alpha_s - \alpha) \\ \dot{Z} &= -\rho_a Z + \rho_a p^2(\alpha_s - \alpha)^2\end{aligned}\tag{A2-4}$$

Appendix 3

In the framework of two-step model B, the basic kinetic equations of the oxygen isotope redistribution in the “gas–solid state” system (6) are as follows:

$$\begin{aligned}\dot{\alpha} &= \rho_{as} \left(\frac{1}{2} \alpha_a + \frac{1}{2} \alpha_s - \alpha \right) \\ \dot{Z} &= \rho_{as} (\alpha_a \alpha_s - C_{36}) - 2\alpha \dot{\alpha}\end{aligned}\tag{A3-1}$$

Since in the framework of the two-step model B the “intermediate” particle is the oxygen adatom, (O)_a, the IQS condition is the following:

$$\rho_{as} (\alpha_a - \alpha) = \rho_i (\alpha_s - \alpha_a)\tag{A3-2}$$

Using (A3-2), we get the ¹⁸O oxygen isotope fraction, α_a , for adatoms as the following:

$$\begin{aligned}\alpha_a &= \alpha + p(\alpha_s - \alpha) \\ p &= \frac{\rho_i}{\rho_{as} + \rho_i} = \frac{\alpha_a - \alpha}{\alpha_s - \alpha}\end{aligned}\tag{A3-3}$$

Taking into account (A3-3) for (A3-1), we get the following:

$$\begin{aligned}\dot{\alpha} &= \frac{1}{2} \rho_{as} (p+1)(\alpha_s - \alpha) \\ \dot{Z} &= -\rho_{as} Z + \rho_{as} p(\alpha_s - \alpha)^2\end{aligned}\tag{A3-4}$$

Appendix 4

In the framework of the two-step model with distributed rates, the basic kinetic equations of the oxygen isotope redistribution in the “gas–solid state” system (6) are as follows:

$$\begin{aligned}\dot{\alpha} &= \sum_{k=1}^K \rho_{ak} (\alpha_{ak} - \alpha) \\ \dot{Z} &= \sum_{k=1}^K \rho_{ak} (\alpha_{ak}^2 - C_{36}) - 2\alpha \dot{\alpha}\end{aligned}\tag{A4-1}$$

where α_{ak} – ^{18}O oxygen isotope fraction in k -centres of the adsorption layer, ρ_{ak} – dissociative adsorption rate on the k -centre of adsorption on the surface.

Since in the framework of the two-step model with distributed rates the “intermediate” particle is the oxygen adatom, $(\text{O})_{ak}$, the IQS condition is the following:

$$\rho_{ak} (\alpha_{ak} - \alpha) = \rho_{ik} (\alpha_s - \alpha_{ak})\tag{A4-2}$$

where ρ_{ik} – incorporation rate of the oxygen k -adatom.

Using (A4-2), we obtain the ^{18}O oxygen isotope fraction, α_a , for adatoms as the following:

$$\begin{aligned}\alpha_{ak} &= \alpha + p(\alpha_s - \alpha) \\ p &= \frac{\rho_{ik}}{\rho_{ak} + \rho_{ik}} = \frac{\alpha_{ak} - \alpha}{\alpha_s - \alpha}\end{aligned}\tag{A4-3}$$

Taking into account (A4-3) for (A4-1), we get the following:

$$\begin{aligned}\dot{\alpha} &= \sum_{k=1}^K g_k p_k \rho_{ak} (\alpha_s - \alpha) \\ \dot{Z} &= -\sum_{k=1}^K g_k \rho_{ak} Z + \sum_{k=1}^K g_k p_k^2 \rho_{ak} (\alpha_s - \alpha)^2\end{aligned}\tag{A4-4}$$

where g_k – fraction of k -centres of adsorption on the surface, p_k – possibility of incorporation of the k -adatom.

Appendix 5

In the framework of the model with the dissociation step, the basic kinetic equations of the oxygen isotope redistribution in the “gas–solid state” system (6) are as follows:

$$\begin{aligned}\dot{\alpha} &= \rho_{2a}(\alpha_{2a} - \alpha) \\ \dot{Z} &= \rho_{2a}(\alpha_{2a}^2 - C_{36}) - 2\alpha\dot{\alpha}\end{aligned}\quad (\text{A5-1})$$

where α_{2a} – ^{18}O oxygen isotope fraction in the adsorption layer.

Since in the framework of the model with the dissociation step the “intermediate” particles are the two-atom oxygen complex, $(\text{O}_2)_{as}$, and the oxygen adatom, $(\text{O})_a$, the IQS condition is the following:

$$\begin{cases} \rho_{2a}(\alpha_{2a} - \alpha) = \rho_{ds}(\alpha_s - \alpha_{2a}) + (2\rho_{da} + \rho_{ds})(\alpha_a - \alpha_{2a}) + \rho_i(\alpha_s - \alpha_a) \\ \rho_{2a}(\alpha_{2a} - \alpha) + (2\rho_{da} + \rho_{ds})(\alpha_a - \alpha_{2a}) = \rho_i(\alpha_s - \alpha_a) \end{cases}\quad (\text{A5-2})$$

Using (A5-2), we obtain the ^{18}O oxygen isotope fraction, α_a , for adatoms as the following:

$$\begin{aligned}\alpha_a &= \alpha + p'(\alpha_s - \alpha) \\ p' &= \frac{\rho_{ds}(2\rho_{da} + 2\rho_i + \rho_{ds}) + \rho_i(\rho_{2a} + 2\rho_{da})}{\rho_{2a}(2\rho_{da} + \rho_i) + \rho_{ds}(\rho_{2a} + 2\rho_{da} + 2\rho_i) + 2\rho_{da}\rho_i} = \frac{\alpha_a - \alpha}{\alpha_s - \alpha}\end{aligned}\quad (\text{A5-3})$$

where p' – possibility of incorporation.

The ^{18}O oxygen isotope fraction, α_{2a} , for the two-atom complexes is the following:

$$\begin{aligned}\alpha_{2a} &= \alpha + p(\alpha_s - \alpha) \\ p &= \frac{\rho_{ds}(2\rho_{da} + 2\rho_i + \rho_{ds}) + 2\rho_{da}\rho_i}{\rho_{2a}(2\rho_{da} + \rho_i) + \rho_{ds}(\rho_{2a} + 2\rho_{da} + 2\rho_i) + 2\rho_{da}\rho_i} = \frac{\alpha_a - \alpha}{\alpha_s - \alpha}\end{aligned}\quad (\text{A5-4})$$

Taking into account (A5-4) for (A5-1), we get the following:

$$\begin{aligned}\dot{\alpha} &= \rho_{2a}p(\alpha_s - \alpha) \\ \dot{Z} &= -\rho_{2a}Z + \rho_{2a}p^2(\alpha_s - \alpha)^2\end{aligned}\quad (\text{A5-5})$$