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Isotope Exchange between NO and H_2O on a Platinum-Containing Catalyst Based on Fiberglass

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Abstract—The dynamics of ^{18}O isotope exchange between NO or H_2O and a catalyst and the dynamics of ^{18}O label transfer from NO to H_2O have been studied under conditions of sorption–desorption equilibrium. The occurrence of a reaction of oxygen exchange between NO and water sorbed in the bulk of the catalyst was detected. This reaction occurs at platinum sites with the participation of acid sites of the glass matrix. The rate constants of the reaction of NO with platinum sites and the diffusion coefficients of water in the bulk of the glass matrix are evaluated.

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INTRODUCTION

The selective catalytic reduction of nitrogen oxides with hydrocarbons in an excess of oxygen (**deNO$_x$**) is of considerable current interest to researchers because this is one of the most efficient techniques for the removal of nitrogen oxides from waste gases (exhaust gases). As a rule, supported catalysts based on aluminosilicates (zeolites or composite materials) are used as deNO$_x$ catalysts. A comparatively new class of catalysts based on fiberglass materials containing small metal amounts, which also exhibit sufficiently high activity in the deNO$_x$ reaction, has attracted increasing interest in the past few years [1].

Traditionally, it is believed that transition metal cations are the active components of deNO$_x$ catalysts. The reaction occurs through the formation of [NO$_x$] surface intermediates, which interact with the hydrocarbon molecule to give rise to a reaction sequence of nitrogen- and carbon-containing complexes. This reaction sequence results in the release of N_2, CO_2, and H_2O [2–7]. At the same time, the results of our studies demonstrated that, along with metal particles, the OH groups of the support can also play a considerable role in the deNO$_x$ reaction. For example, in a mechanistic study of this reaction on a CoZSM-5 catalyst, it was found that the protonated $NO_2^{\delta+}$ species formed at neighboring Co^{2+}–OH sites is a key intermediate (most active toward hydrocarbons) [8]. In fiberglass catalysts, metal is finely dispersed, and they are surrounded by a great number of OH groups. In this case, it is believed that the probability of formation of protonated NO$_x$ complexes increases even in the absence of oxygen in the feed gas. In this context, the mechanism and kinetics of the reactions of NO with fiberglass catalysts are of special interest.

Carrying out our studies, we faced the following problem: Because of a too low concentration of sorbed NO, traditional approaches to studying sorption mechanisms with the use of a relaxation kinetic technique and IR spectroscopy were found to be inadequately informative. In the former case, the relaxation times were comparable to the time resolution of the experimental procedure. In the latter case, the sensitivity of IR spectroscopy was insufficient for the identification of the resulting intermediate complexes. In this case, the isotopic technique gave the best results. We found that, in the course of NO sorption, isotope exchange between NO and catalyst oxygen occurred; in this process, a portion of labeled oxygen atoms can pass into water. We studied the transfer dynamics of the ^{18}O label from NO to a catalyst and water in various fiberglass catalyst samples (without platinum and with supported platinum). We evaluated the rate constant of the reaction of NO with platinum sites and proposed a reaction scheme of oxygen exchange. On this basis, we can draw conclusions on the nature of intermediates formed in the reaction of NO with a catalyst.

EXPERIMENTAL

Preparation of Fiberglass Catalysts

The physicochemical properties and structure of leached silica fiberglass used for catalyst preparation were studied previously using a set of physicochemical techniques (BET; IR spectroscopy; TEM; and ^{29}Si, ^{23}Na, ^{27}Al, ^{133}Cs, and ^{129}Xe NMR spectroscopy) [9, 10]. It was found that the chemical composition of a matrix formed upon the complete leaching of sodium silicate glass fibers corresponded to SiO_2. This matrix consisted of disordered (relatively labile) fragments. However, ordered silicon–oxygen tetrahedron layers alter-

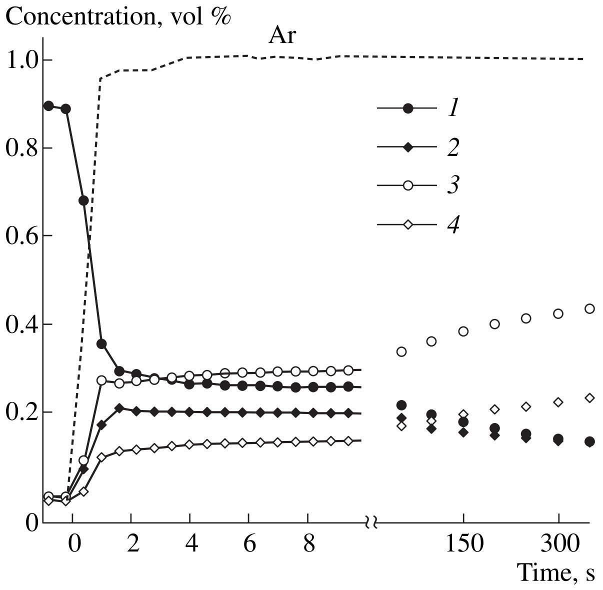


Fig. 1. The time dependence of the concentrations of isotopic NO molecules at the reactor outlet observed on the replacement of $^{14}N^{16}O$ by $^{15}N^{18}O$ in a mixture of NO + He passed through the Pt-containing catalyst: (*1*) $^{14}N^{16}O$, (*2*) $^{15}N^{16}O$, (*3*) $^{14}N^{18}O$, and (*4*) $^{15}N^{18}O$.

nating with narrow cavities containing a large amount of hydroxyl groups can be distinguished in an individual structural fragment of this matrix [9]. According to TPD data, the residual concentration of OH groups at 300–400°C was about 1000 μmol/g (or 6×10^{20} molecule/g).

The fiberglass catalysts used in this study were prepared by introducing platinum ions from ammonia salt solutions using ion exchange. Thereafter, the fiberglass was washed with deionized water for removing weakly bound platinum compounds; next, it was dried and calcined at 300°C. The amount of platinum in the fiberglass was determined by atomic absorption spectrometry; it was equal to ~0.05 wt % (or 15×10^{17} molecule/g). According to XPS data [11], platinum penetrates into glass fiber at a depth of about 100 Å; platinum microparticles are in a positively charged rather than metallic state (isolated Pt^{2+} ions or small clusters). The procedure for preparing Pt-containing catalysts was described in detail elsewhere [11].

EXPERIMENTAL PROCEDURE

The experimental procedure consisted in the following: A mixture of NO + He, NO + H_2O + He, or H_2O + He was passed through a catalyst bed. After reaching an adsorption–desorption equilibrium, the mixture was stepwise changed to a chemically identical but isotopically different mixture and the changes in the concentration of isotopic molecules at the reactor outlet with time were measured.

Three types of experiments were performed on two samples of fiberglass catalysts without platinum and with 0.05% platinum as follows:

(a) the replacement of $^{14}N^{16}O$ + He by $^{15}N^{18}O$ + He;

(b) the replacement of $^{14}N^{16}O$ + $H_2{}^{16}O$ + He by $^{15}N^{18}O$ + $H_2{}^{16}O$ + He;

(c) the replacement of $H_2{}^{16}O$ + He by $H_2{}^{18}O$ + He.

In case (a), the catalyst samples were heated in a mixture of O_2 + He at 400°C for 1 h before experiments; in cases (b) and (c), the catalyst samples were additionally pretreated in water vapor.

The mixtures were changed using a pneumatic valve with a time resolution of ~0.1 s. The experiments were performed in a flow system with a tubular reactor under plug-flow conditions. A small amount (0.16%) of argon was added to the isotope-containing mixture in order to evaluate the time of reactor and line purging. For saturation with water vapor, the initial gases (NO + He or pure helium) were passed through bubblers with ordinary or labeled water at room temperature (~20°C) and atmospheric pressure. According to chromatographic analysis data, the mixtures were incompletely saturated with water vapor so that the concentration of H_2O was ~1.5% (the vapor pressures of labeled and unlabeled water were taken equal). The gas flow rate was 2 ml/s; the catalyst weight was 0.2 g; the reactor temperature was 400°C. The concentration of NO was 0.9 vol %. The ^{15}N and ^{18}O enrichments of labeled NO were 38 and 96%, respectively. The ^{18}O enrichment of labeled water was 80.5%.

Before loading, the catalyst as initial fiberglass was separated into individual fibers for the more uniform access of a gas to the surface of the fibers. The fiber diameter was ~10 μm [9].

RESULTS

Replacement of $^{14}N^{16}O$ + He by $^{15}N^{18}O$ + He. Figure 1 shows the time dependence of the concentrations of isotopic NO molecules at the reactor outlet with a Pt-containing catalyst. An abrupt change in the concentrations of all of the NO isotopomers followed by slow relaxation to a new isotopic composition of the inlet mixture was observed in the experiments. First, an abrupt change in the concentration of $^{15}N^{16}O$ (whose concentration in the inlet mixture was negligibly small) should be noted, which is indicative of a rapid reaction of NO with the catalyst accompanied by isotope exchange between the resulting adsorbed complexes and the oxygen atoms of the catalyst. The rate of isotope exchange decreased as ^{16}O in the catalyst was replaced by ^{18}O, and we observed a slow decrease in the concentration of $^{15}N^{16}O$.

Figure 2 illustrates changes in the isotope fractions $\alpha_{NO}^{15}(t)$ and $\alpha_{NO}^{18}(t)$ $\left(\alpha_{NO}^{15} = \frac{^{15}N^{16}O + {}^{15}N^{18}O}{\sum {}^{i}N^{j}O},\ \alpha_{NO}^{18} =\right.$

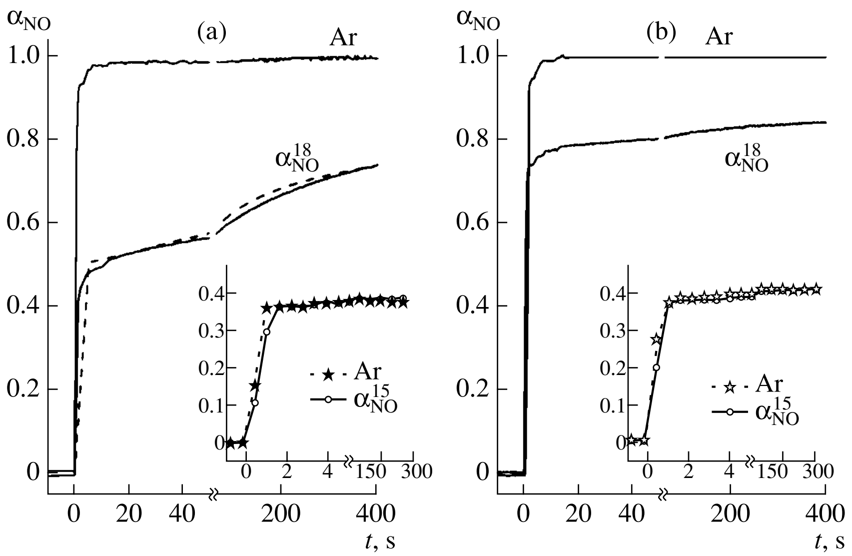


Fig. 2. The time dependence of the ^{18}O and (insets) ^{15}N isotope fractions on the replacement of $^{14}N^{16}O$ + He by $^{15}N^{18}O$ + He observed on (a) the Pt-containing catalyst (solid and dashed lines indicate experimental and calculated data, respectively) and (b) parent fiberglass.

$\left.\frac{^{14}N^{18}O + {}^{15}N^{18}O}{\sum {}^{i}N^{j}O}\right)$ in the outlet mixture in the experiments performed on a Pt-containing catalyst (Fig. 2a) and on a sample of the parent fiberglass (Fig. 2b). Unlike ^{18}O, the dynamics of ^{15}N isotope response was not complicated by isotope exchange with the catalyst but depended on the sorption–desorption rate of NO. It is well known that the amount of an adsorbed substance can be evaluated from the area between the elution curve and the isotope response curve: $N_{NO} = \frac{C_{NO}U}{\overset{15}{\alpha}_{NO\ inlet}}S$ (where N_{NO} is the amount of sorbed NO, S is the area between the response curves, C_{NO} is the NO concentration in a gas phase, U is the flow rate, and $\overset{15}{\alpha}_{NO\ inlet}$ is the ^{15}N enrichment of the inlet mixture). In our experiments performed with both the catalyst and the parent fiberglass, the shift of the $\overset{15}{\alpha}_{NO}(t)$ curve relative to the normalized response curve for Ar was comparable to the time resolution of the mass spectrometer, which was equal to 0.6 s. In this case, the area and, correspondingly, the amount of sorbed NO can be estimated only from the upper limit of $N_{NO} < 14 \times 10^{17}$ molecule/g, which does not exceed the number of platinum sites in the sample.

Comparing the $\overset{15}{\alpha}_{NO}(t)$ and $\overset{18}{\alpha}_{NO}(t)$ response curves, we can conclude that, at $t \geq 1.2$ s, the dynamics of $\overset{18}{\alpha}_{NO}(t)$ response depends only on isotope exchange with oxygen of the catalyst. Then, based on balance relations between the amounts of ^{18}O at the reactor inlet and outlet, we can calculate the rate of ^{18}O transfer to the catalyst: $W_{^{18}O_{Cat}} = (\overset{18}{\alpha}_{NO\ inlet} - \overset{18}{\alpha}_{NO})UC_{NO}$ (Fig. 3). The total amount of exchangeable oxygen in the catalyst can be evaluated by approximating the resulting rates of transfer to longer times (in this case, a function of the form Ae^{-kt} was used as an approximation function). This amount was about 10^{21} atom/g, which is comparable with the total amount of hydroxyl groups in fiberglass. It can be seen in Fig. 3 that the initial rate of

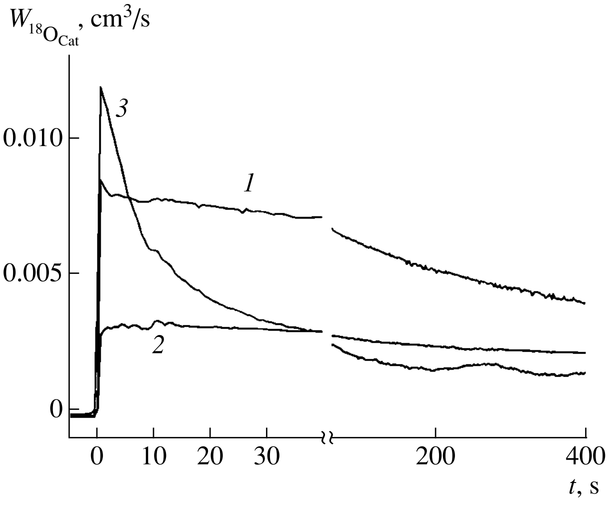


Fig. 3. The time dependence of the rate of ^{18}O transfer from NO to the catalyst on the replacement of $^{14}N^{16}O$ + He by $^{15}N^{18}O$ + He on (*1*) the Pt-containing catalyst and (*2*) the support and (*3*) on the replacement of $^{14}N^{16}O + H_2{}^{16}O$ + He by $^{15}N^{18}O + H_2{}^{16}O$ + He on the Pt-containing catalyst.

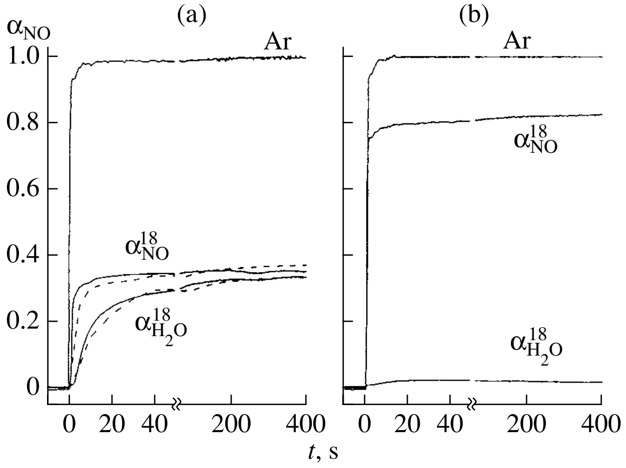


Fig. 4. The time dependence of the ^{18}O isotope fractions in NO and H_2O on the replacement of $^{14}N^{16}O + H_2{}^{16}O$ + He by $^{15}N^{18}O + H_2{}^{16}O$ + He observed on (a) the Pt-containing catalyst (solid and dashed lines indicate experimental and calculated data, respectively) and (b) parent fiberglass.

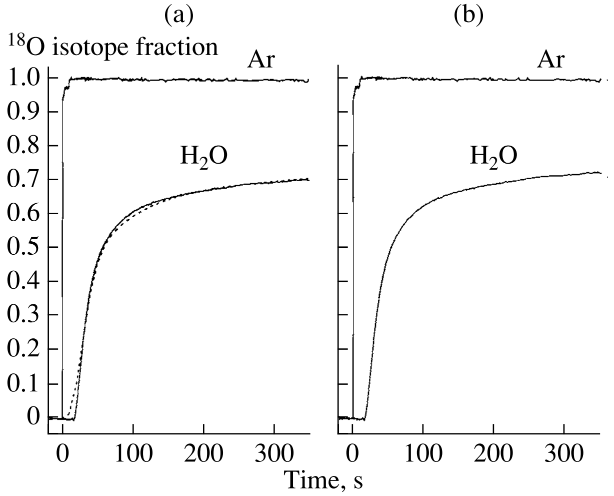


Fig. 5. The time dependence of the ^{18}O isotope fractions in H_2O on the replacement of $H_2{}^{16}O$ + He by $H_2{}^{18}O$ + He observed on (a) the Pt-containing catalyst (solid and dashed lines indicate experimental and calculated data, respectively) and (b) the support.

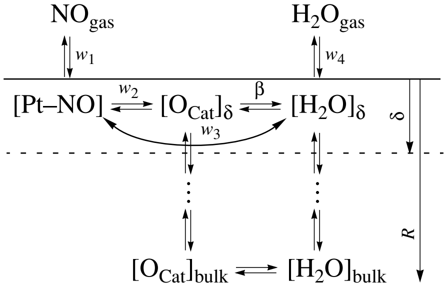
^{18}O transfer (curve *1*) on the platinum-containing catalyst was higher than that on the parent fiberglass (curve *2*) by a factor of 2.5. That is, the introduction of platinum into fiberglass increased the rate of NO exchange with oxygen of the catalyst. Therefore, we can conclude that NO penetrates into the bulk of fiberglass and interacts with platinum sites.

Replacement of $^{14}N^{16}O + H_2{}^{16}O$ + He by $^{15}N^{18}O$ + $H_2{}^{16}O$ + He. The presence of water in a mixture had no significant effect on the dynamics of response for labeled nitrogen (as previously, the shift of the $\alpha^{15}_{NO}(t)$ curve with reference to the elution curve is comparable with the time resolution of the mass spectrometer). However, in this case, the dynamics of response for labeled oxygen on the Pt-containing catalyst dramatically changed (Fig. 4a). It can be seen that the ^{18}O content of NO at the reactor outlet was much lower than that in a mixture of NO + He. In this case, we observed the ^{18}O label as a constituent of water and an increase in the rate of ^{18}O transfer to the catalyst: $W_{^{18}O_{Cat}} = (\alpha^{18}_{NO\,inlet} C_{NO} - (\alpha^{18}_{NO} C_{NO} + \alpha^{18}_{H_2O} C_{H_2O}))U$ (Fig. 3, curve *3*). Note that these effects were not observed on the pure support: the concentration of ^{18}O in water was negligibly small, and the $\alpha^{18}_{NO}(t)$ response curves obtained in NO + He (Fig. 2b) and NO + H_2O + He (Fig. 4b) mixtures coincided. We can conclude that platinum sites also play a key role in the mechanism of isotope exchange between NO and water.

Replacement of $H_2{}^{16}O$ + He by $H_2{}^{18}O$ + He. The isotope fraction of ^{18}O in H_2O at the reactor outlet was close to zero over the first 20 s after the supply of labeled water to the reactor; that is, ^{18}O was transferred almost completely to the catalyst (Fig. 5a). Next, the rate of this transfer dramatically decreased. As can be seen in Fig. 5, the presence of platinum had no effect on the dynamics of ^{18}O replacement in H_2O and fiberglass (cf. Figs. 5a and 5b). Based on the shape of the $\alpha^{18}_{H_2O}(t)$ response curve, we can conclude that the dynamics of ^{18}O transfer from water vapor to the catalyst depends on two processes (rapid and slow processes). The rapid transfer of the label is due to water sorption/desorption from the bulk of the catalyst, whereas the slow transfer is due to isotope exchange with oxygen of the catalyst. It is most likely that oxygen exchange between sorbed water and the OH groups of the glass matrix occurs.

SIMULATION AND DISCUSSION

Based on experimental results and current concepts of the structure of the catalyst, the isotope exchange of NO with oxygen of the catalyst and water can be schematically represented as follows: Sorbed NO reacts with Pt^{2+}; in the course of this interaction, the exchange of NO with catalyst oxygen atoms bound to platinum sites occurs. Taking into account that platinum in fiberglass catalysts is finely dispersed and the platinum particles are surrounded by a large amount of OH groups, theoretically, two modes of oxygen exchange between NO and active sites are conceivable: (a) with oxygen directly bound to platinum and (b) with OH groups localized in the immediate vicinity of platinum sites. Unlike platinum sites, which are stable, the concentration of OH groups in fiberglass can change under the action of temperature and water. Based on bond strengths, the probability of exchange in accordance with the latter mode is higher. The ^{18}O label diffused from platinum sites deep into the fiberglass without the participation of NO, most likely, by oxygen exchange between neighboring hydroxyl groups. The transfer of labeled oxygen deep into the fiberglass can be considered as an analogy of diffusion. It is evident that, if the ^{18}O label from NO passes into the catalyst (most likely, into the OH groups of the catalyst) and, in turn, the catalyst can exchange oxygen atoms with water sorbed in the bulk of the fiberglass, labeled oxygen atoms can thus pass from NO into water. At the same time, it is believed that direct exchange between Pt–NO and water sorbed by the catalyst can occur. Then, the generalized scheme of oxygen exchange among NO, the catalyst, and water can be represented as follows:



Taking into account that the depth δ of a layer in which platinum is localized is a few thousandths of the fiber radius R ($\delta \le 0.002R$), the amount of exchangeable oxygen atoms, including [Pt–NO], $[O_{Cat}]_\delta$, and $[H_2O]_\delta$, in this layer can be considered as a negligibly small value, as compared with the amounts of oxygen in $[H_2O]_{bulk}$ and, especially, in $[O_{Cat}]_{bulk}$ in the bulk of the fiber. Then, using a quasi-steady-state approximation for calculating the isotope fraction of ^{18}O in [Pt–NO] $\left(\alpha^{18}_{[PtNO]} = \frac{w_1\alpha^{18}_{NO_{gas}} + w_2\alpha^{18}_{[O_{Cat}]_\delta} + w_3\alpha^{18}_{[H_2O]_\delta}}{w_1 + w_2 + w_3}\right)$ and assuming $\alpha^{18}_{[O_{Cat}]_\delta} = \alpha^{18}_{[O_{Cat}]}\Big|_{\eta = 0}$ and $\alpha^{18}_{[H_2O]_\delta} = \alpha^{18}_{[H_2O]}\Big|_{\eta = 0}$, the general model of ^{18}O transfer, which corresponds to the above scheme, can be written in the form

$$\frac{\partial\alpha^{18}_{NO_{gas}}}{\partial t} + \frac{U}{V}\frac{\partial\alpha^{18}_{NO_{gas}}}{\partial\xi}$$

$$= -\frac{g}{C_{NO_{gas}}V}[w_{12}(\alpha^{18}_{NO_{gas}} - \alpha^{18}_{[O_{Cat}]}\Big|_{\eta = 0})$$

$$+ w_{13}(\alpha^{18}_{NO_{gas}} - \alpha^{18}_{[H_2O]}\Big|_{\eta = 0}),$$

$$\frac{\partial\alpha^{18}_{H_2O_{gas}}}{\partial t} + \frac{U}{V}\frac{\partial\alpha^{18}_{H_2O_{gas}}}{\partial\xi}$$

$$= -\frac{g}{C_{H_2O_{gas}}V}w_4(\alpha^{18}_{H_2O_{gas}} - \alpha^{18}_{[H_2O]}\Big|_{\eta = 0}),$$

$$\frac{\partial\alpha^{18}_{[O_{Cat}]}}{\partial t} = \frac{D_1}{R^2}\frac{\partial^2\alpha^{18}_{[O_{Cat}]}}{\partial\eta^2} - \beta\frac{\theta_{[H_2O]}}{\theta_{[O_{Cat}]}}(\alpha^{18}_{[H_2O]} - \alpha^{18}_{[O_{Cat}]}),$$

$$\frac{\partial\alpha^{18}_{[H_2O]}}{\partial t} = \frac{D_2}{R^2}\frac{\partial^2\alpha^{18}_{[H_2O]}}{\partial\eta^2} - \beta(\alpha^{18}_{[O_{Cat}]} - \alpha^{18}_{[H_2O]}),$$

$$w_{12} = \frac{w_1 w_2}{w_1 + w_2 + w_3}, \quad w_{13} = \frac{w_1 w_3}{w_1 + w_2 + w_3}.$$

Initial conditions:

$$t = 0:\ \alpha^{18}_{NO_{gas}} = \alpha^{18}_{H_2O_{gas}} = \alpha^{18}_{[O_{Cat}]} = \alpha^{18}_{[H_2O]} = 0.$$

Boundary conditions:

$$\xi = 0:\ \alpha^{18}_{NO_{gas}} = \alpha^{18}_{NO,\,inlet}, \quad \alpha^{18}_{H_2O_{gas}} = \alpha^{18}_{H_2O,\,inlet};$$

$$\eta = 0:$$

$$w_{12}(\alpha^{18}_{NO_{gas}} - \alpha^{18}_{[O_{Cat}]}\Big|_{\eta = 0}) = \theta_{[O_{Cat}]}\left[\frac{D_1}{R^2}\frac{\partial\alpha^{18}_{[O_{Cat}]}}{\partial\eta}\Bigg|_{\eta = 0}\right.$$

$$\left. - \beta\frac{\theta_{[H_2O]}}{\theta_{[O_{Cat}]}}(\alpha^{18}_{[H_2O]}\Big|_{\eta = 0} - \alpha^{18}_{[O_{Cat}]}\Big|_{\eta = 0})\right],$$

$$w_4(\alpha^{18}_{H_2O_{gas}} - \alpha^{18}_{[H_2O]}\Big|_{\eta = 0}) + w_{13}(\alpha^{18}_{NO_{gas}} - \alpha^{18}_{[H_2O]}\Big|_{\eta = 0})$$

$$= \theta_{[H_2O]}\left[\frac{D_2}{R^2}\frac{\partial\alpha^{18}_{[H_2O]}}{\partial\eta}\Bigg|_{\eta = 0}\right.$$

$$\left. - \beta(\alpha^{18}_{[O_{Cat}]}\Big|_{\eta = 0} - \alpha^{18}_{[H_2O]}\Big|_{\eta = 0})\right].$$

This model takes into account changes in the concentration of the oxygen label with time (t) along the length (ξ) of the catalyst bed and in depth (η) of the fiber. Here, $C_{NO_{gas}}$ and $C_{H_2O_{gas}}$ are the concentrations of NO and H_2O, respectively, in a gas phase (mol/cm^3); $\alpha^{18}_{NO_{gas}}$ and $\alpha^{18}_{H_2O_{gas}}$ are the corresponding isotope fractions; $\theta_{[H_2O]}$ and $\alpha^{18}_{[H_2O]}$ are the concentration of sorbed water (mol/g) and the fraction of ^{18}O in it, respectively; $\theta_{[O_{Cat}]}$ and $\alpha^{18}_{[O_{Cat}]}$ are the concentration of exchangeable oxygen in the catalyst (mol/g) and the fraction of ^{18}O in it, respectively; U is the flow rate (cm^3/s); V is the reaction space volume (cm^3); g is the catalyst weight (g); w_1 is the rate of NO sorption (mol s^{-1} g^{-1}); w_2 is the rate of oxygen exchange of [Pt–NO] with $[O_{Cat}]_\delta$ (mol s^{-1} g^{-1}); w_3 is the rate of oxygen exchange of [Pt–NO] with $[H_2O]_\delta$ (mol s^{-1} g^{-1}); w_4 is the rate of sorption/desorption of water (mol s^{-1} g^{-1}); D_1 is the diffusion coefficient of oxygen atoms of the catalyst (cm^2/s); D_2 is the diffusion coefficient of water in the bulk of fiberglass (cm^2/s); R is the fiber radius (cm); and β is the coefficient of oxygen exchange between $[O_{Cat}]$ and $[H_2O]$ (s^{-1}).

In terms of this model, we performed a numerical analysis of isotope response on the replacement of $^{14}N^{16}O$ by $^{15}N^{18}O$ in a mixture of NO + He or $H_2{}^{16}O$ by $H_2{}^{18}O$ in a mixture of H_2O + He. In the former case, the sought model parameters were w_1 and D_1 and the value of $\theta_{[O_{Cat}]}$ was refined (β, w_{13}, and w_4 were taken equal to zero); in the latter case, the values of w_2, $\theta_{[H_2O]}$, D_2, and β ($w_{12} = 0$) were found.

The calculated values of the sought parameters were the following:

$$w_{12} = 2.5 \times 10^{-6}\ \text{mol g}^{-1}\ \text{s}^{-1};$$

$$w_4 = 1.4 \times 10^{-5}\ \text{mol g}^{-1}\ \text{s}^{-1};$$

$$D_1 = 3 \times 10^{-9}\ \text{cm}^2/\text{s}; \quad D_2 = 2 \times 10^{-8}\ \text{cm}^2/\text{s};$$

$$\theta_{[O_{Cat}]} = 0.5 \times 10^{-2}\ \text{mol/g};\ \beta = 0.02\ \text{s}^{-1};$$

$$\theta_{[H_2O]} = 0.44 \times 10^{-3}\ \text{mol/g}.$$

The results of the simulation indicated that this model adequately describes both the dynamics of NO isotope exchange with the catalyst and the exchange of H_2O with the catalyst. As can be seen in Figs. 2a and 4a, the experimental and calculated response curves practically coincided in both cases. Note that the found diffusion coefficient of water is higher than diffusion coefficients in solids by several orders of magnitude. It is believed that, in this case, the diffusion of water (whose molecule exhibits a high dipole momentum) is stimulated by the interaction with the OH groups of fiberglass.

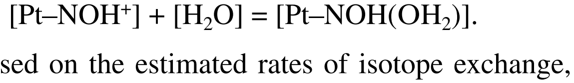
With the use of the above model parameters w_{12}, w_4, D_1, D_2, β, $\theta_{[O_{Cat}]}$, and $\theta_{[H_2O]}$, we simulated the dynamics of ^{18}O transfer from NO to H_2O. In this simulation, we considered two variants: (a) the rate of exchange between [Pt–NO] and $[H_2O]_\delta$ is zero ($w_{13} = 0$) and (b) exchange between these complexes takes place ($w_{13} > 0$). In the former case, the calculated concentration of labeled oxygen in water was much lower than the experimental value; that is, the transfer of the label only through the oxygen of the catalyst cannot provide the experimentally observed rate of exchange between NO and H_2O. In the latter case, when we took into account the possibility of the direct exchange of [Pt–NO] and $[H_2O]_\delta$, we managed to describe experimental response curves (Fig. 4a). The calculated value of w_{13} was

$$w_{13} = (9 \pm 2) \times 10^{-6}\ \text{mol s}^{-1}\ \text{g}^{-1}.$$

In accordance with the results of the simulation, the observed dynamics of ^{18}O transfer from NO to H_2O can be explained as follows: Because the amount of exchangeable oxygen in the glass matrix was very large ($[O_{Cat}] \gg [H_2O]$), the ^{18}O isotope fraction in $[O_{Cat}]$ remained practically unchanged (equal to zero) during the entire experiment. Consequently, the rate of label transfer via the reaction path $N^{18}O_{gas} \longrightarrow [Pt{-}N^{18}O] \longrightarrow [^{18}O_{Cat}] \longrightarrow [H_2{}^{18}O] \longrightarrow H_2{}^{18}O_{gas}$ was negligibly low. The observed dynamics of isotope response in H_2O primarily depended on the rate of label transfer via the second path $N^{18}O_{gas} \longrightarrow [Pt{-}N^{18}O] \longrightarrow [H_2{}^{18}O] \longrightarrow H_2{}^{18}O_{gas}$. The direct $[PtNO]{-}[H_2O]_\delta$ exchange and water diffusion, which is responsible for the rapid migration of the label deep into glass fiber, resulted in a sharp peak of the rate of ^{18}O transfer to the catalyst, which was observed at the initial period. The rate of water diffusion was high, as compared with the rate of $[PtNO]{-}[H_2O]_\delta$ exchange, so that the isotope fraction in $[H_2O]_\delta$ remained equal to zero for a few seconds after the supply of labeled oxygen to the reactor and ^{18}O almost completely passed into the bulk of fiberglass. The rate of the $[H_2{}^{18}O] \longrightarrow H_2{}^{18}O_{gas}$ transfer gradually increased as water in the bulk of the catalyst was replaced, and the rate of label transfer via the second path stabilized after a lapse of ~50 s from the point in time at which labeled NO arrived at the reactor; the observed concentrations of $N^{18}O_{gas}$ and $H_2{}^{18}O_{gas}$ became approximately constant.

Thus, based on the results of the simulation, we can draw the following conclusion: The isotope-exchange reaction of [Pt–NO] complexes with water sorbed in the bulk of fiberglass makes the main contribution to the apparent rate of ^{18}O transfer from NO to water. Taking into account the fact that the direct interaction of Pt–NO with H_2O is improbable, the mechanism of this exchange can be represented as follows: strong $\mathrm{Al{-}\overset{H}{\overset{|}{O}}{-}Si}$ acid sites localized in the immediate vicinity of platinum sites interact with [Pt–NO] to form the protonated complex [Pt–NOH$^+$]. Water adds to [Pt–NOH$^+$] to give the intermediate complex [Pt–NOH(OH_2)], in which isotope exchange between oxygen atoms can readily occur by proton transfer. Labeled oxygen passes into water upon the degradation of this complex. On this basis, the reaction scheme of the interaction of NO with the catalyst can be represented as follows:

(1) $Pt^{2+} + NO = [Pt{-}NO]$;



(2) $[Pt{-}NO] + [\mathrm{Al{-}\overset{H}{\overset{|}{O}}{-}Si}] = [Pt{-}NOH^+] + [Si{-}O{-}Al]$;

(3) $[Pt{-}NOH^+] + [H_2O] = [Pt{-}NOH(OH_2)]$.

Based on the estimated rates of isotope exchange, the apparent rate constant of the interaction of NO with platinum sites can be evaluated from the lower limit. Expressing the rate constant of the first step as

$$k_1 = \frac{w_1}{C_{\mathrm{NO}}L}$$

(where L is the number of platinum atoms per gram of the catalyst) and taking into account that $w_1 > w_{13}$, we obtain $k_1 > 400\ \mathrm{s}^{-1}$ per platinum atom.

Thus, based on the experimental data, we found that NO molecules actively interact with platinum sites localized in the bulk of a glass matrix at a depth of <100 Å. The rate constant of this interaction is higher than $4 \times 10^2\ \mathrm{s}^{-1}$. The resulting PtNO complexes can exchange oxygen atoms with both the OH groups of the glass matrix and water sorbed in the bulk of fiberglass. It is believed that the interaction of [Pt–NO] with a strong acid site to form the protonated complex [Pt–NOH^+] is a key step in the mechanism of oxygen exchange between PtNO and sorbed water.

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