ISSN 0023-1584, Kinetics and Catalysis, 2012, Vol. 53, No. 1, pp. 107–116. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © N.A. Sadokhina, A.F. Prokhorova, R.I. Kvon, I.S. Mashkovskii, G.O. Bragina, G.N. Baeva, V.I. Bukhtiyarov, A.Yu. Stakheev, 2012, published in Kinetika i Kataliz, 2012, Vol. 53, No. 1, pp. 110–119.

Dependence of the Catalytic Activity of Ag/Al_2O_3 on the Silver Concentration in the Selective Reduction of NO_x with *n*-Hexane in the Presence of H_2

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Received May 11, 2011

Abstract—The activity of 0.25–5% Ag/Al_2O_3 catalysts in the selective catalytic reduction of nitrogen oxides with *n*-hexane under the conditions of promotion with a small amount of H_2 was studied. It was found that, upon the introduction of ~1000 ppm of H_2 into the reaction mixture, the Ag/Al_2O_3 samples containing 1–2% Ag exhibited optimum activity and selectivity. It was established that, in the presence of 1000 ppm of H_2, the rate of the selective catalytic reduction of NO_x was higher by a factor of 10–13, and the onset temperature of the reaction was lower by approximately 100°C. It was found by X-ray photoelectron spectroscopy, temperature-programmed reduction, and UV spectroscopy that the high activity of 1–2% Ag/Al_2O_3 catalysts was due to the presence of small $Ag_n^{\delta+}$ and Ag_m^0 clusters on their surface. A decrease in the concentration of Ag below the optimum value resulted in the predominance of an inactive ionic form on the catalyst surfaces. As the concentration of Ag was increased (>2%), large particles of Ag_2O and Ag^0, which facilitate the oxidation of *n*-C_6H_{14}, were formed to lead to a decrease in selectivity and in the degree of reduction of nitrogen oxides.

DOI: 10.1134/S0023158412010090

INTRODUCTION

The catalytic removal of nitrogen oxides (NO_x = NO + NO_2), which enter the atmosphere with vehicular exhaust, is a problem of considerable current interest in environmental technologies because of the high toxicity of NO_x for human beings and its adverse effect on the environment. The selective catalytic reduction of NO_x with hydrocarbons (HC-SCR of NO_x) is currently one of the most intensively developed methods for removal of nitrogen oxides [1–4]. Catalysts based on silver supported onto aluminum oxide (Ag/Al_2O_3) [5] are promising for practical applications.

Interest in Ag/Al_2O_3 has renewed in the past few years because it was found that the activity of these catalysts at low temperatures of 150–350°C increased upon the addition of H_2 to the reaction mixture [6–8]. This effect is very important for wide use of silver catalysts in the automotive catalytic converters; for this reason, the mechanism of H_2 promotion effect has been intensively studied by different research groups throughout the world.

However, many of the above studies were carried out in the presence of relatively high concentrations of H_2 (>4000 ppm) [9–13]. Therefore, there are serious difficulties in the practical use of this reaction because the real concentration of H_2 in the operation of a diesel engine does not exceed 1000 ppm. Furthermore, either light hydrocarbons (for example, ethane, propane, and butane) [14–17] or hydrocarbons with more than ten carbon atoms per molecule (decane etc.) [18–20] were used as reducing agents for nitrogen oxides, whereas hydrocarbons with five to eight carbon atoms per molecule dominate in the exhaust gases of highly economical lean burn gasoline and diesel engines, which operate with lean fuel–air mixtures. The factors affecting the selectivity of SCR, which is the efficiency of hydrocarbon consumption for the reduction of nitrogen oxides rather than the competing nonselective oxidation of hydrocarbons by atmospheric oxygen, remain unclear.

In this context, the present study of the activity of silver catalysts in the SCR reaction of NO_x in the presence of a small quantity of H_2 (1000 ppm) is of obvious interest. In this study, we used *n*-hexane as the reducing agent for nitrogen oxides; it simulated the composition of the unburned hydrocarbons occurring in the

Test Ag/Al_2O_3 catalysts

Sample	[Ag], wt %	Catalyst weight, g
0Ag	0.00	0.375
0.25Ag	0.25	0.378
0.5Ag	0.50	0.375
0.75Ag	0.75	0.375
1Ag	1.00	0.378
1.25Ag	1.25	0.385
2Ag	2.00	0.385
3Ag	3.00	0.363
5Ag	5.00	0.369

exhaust gases of a gasoline engine. Special attention was given to the selectivity of the SCR of NO_x.

It should be noted that the silver content of the catalysts greatly affects the catalytic activity of Ag/Al_2O_3. According to published data [5, 21–26], the concentration of Ag can be varied over the wide range from 1 to 5% to reach a high conversion of NO_x. It was important to establish whether the activity of catalysts with different Ag contents is related to the structure of their surfaces. To answer this question, we studied the samples by X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), and UV spectroscopy and compared these data with the results of catalytic tests.

EXPERIMENTAL

Catalyst Preparation

A commercial γ-Al_2O_3 support (Sasol, S_{BET} = 152 m^2/g) precalcined in a flow of dry air (300 ml/min) at 550°C for 4 h was used in the preparation of the Ag/Al_2O_3 catalysts containing from 0.25 to 5% Ag (table). The support was impregnated (incipient wetness method) with an aqueous solution of $AgNO_3$. The resulting sample was dried at room temperature and calcined in a flow of dry air (300 ml/min) at 550°C for 4 h. Next, the catalyst was sifted through sieves and the 0.4–1.0 mm size fraction was collected.

Catalytic Activity Measurements

Catalytic activity in the SCR of NO_x with *n*-hexane was measured in a tubular quartz flow reactor (inner diameter of 6 mm). The experiments were carried out on a gas mixture containing 300 ppm of *n*-C_6H_{14}, 300 ppm of NO, 10% CO_2, 7.5% O_2, and 1000 ppm of H_2 in N_2 at a flow rate of 500 ml/min in the temperature range of 100–550°C at a gas hourly space velocity (GHSV) of 60000 h^{-1}—conditions imitating the possible operation of Ag/Al_2O_3 in automotive catalytic converters.

The concentration of *n*-hexane was determined on an LKhM-80 gas chromatograph equipped with a flame-ionization detector and a packed column with Al_2O_3 as a stationary phase, and the concentrations of NO and NO_2 were determined on an Eco Physics CLD 70 S NO/NO_x chemiluminescence gas analyzer.

The conversions of NO_x (X_{NO_x}, %) and *n*-C_6H_{14} ($X_{C_6H_{14}}$, %) were calculated from the following equations:

$$X_{NO_x} = 1 - C_{outNO_x}/C_{inNO},$$

$$X_{C_6H_{14}} = 1 - C_{outC_6N_{14}}/C_{inC_6H_{14}},$$

where C_{in} and C_{out} are the concentrations of the corresponding gases at the reactor inlet and outlet, respectively.

Catalytic activity (A_m, μmol g^{-1} s^{-1}) was calculated as

$$A_m = \frac{0.01 X_{NO_x} C_{inNO} u}{V_m m},$$

where u is the flow rate, ml/s; V_m is the molar gas volume, ml/mol; and m is the catalyst weight, g.

The reaction selectivity (S, mol NO/mol *n*-C_6H_{14}) was calculated using the equation

$$S = \frac{C_{inNO} X_{NO_x}}{C_{inC_6H_{14}} X_{C_6H_{14}}}.$$

The temperatures of the 25% conversion of NO_x (T_{25,NO_x}, °C) and *n*-C_6H_{14} ($T_{25,C_6H_{14}}$, °C) were determined by interpolation of conversion curves to low conversions (Figs. 1 and 2, respectively).

Physicochemical Characterization Techniques

UV spectroscopy. Diffuse reflectance UV spectra were measured on a Shimadzu CS-9001 PC spectrophotometer over the wavelength range of 200–700 nm with a resolution of 1 nm. The scanning rate was 10 nm/s. Before the spectral measurements, the samples were calcined in a flow of dry air at 550°C for 4 h.

Temperature-programmed reduction. Before TPR, the samples (0.1 g) were placed in a U-shaped reactor, heated in a flow of dry air to 450°C at a rate of 5 K/min, and then cooled to 100°C. At 100°C, air was replaced by a flow of Ar and the cooling of the samples to room temperature was continued.

To perform TPR, the samples were heated in a flow of Ar, which contained 5% H_2 (flow rate, 30 ml/min) to 825°C at a rate of 5 K/min. The H_2 uptake was measured with a thermal-conductivity detector.

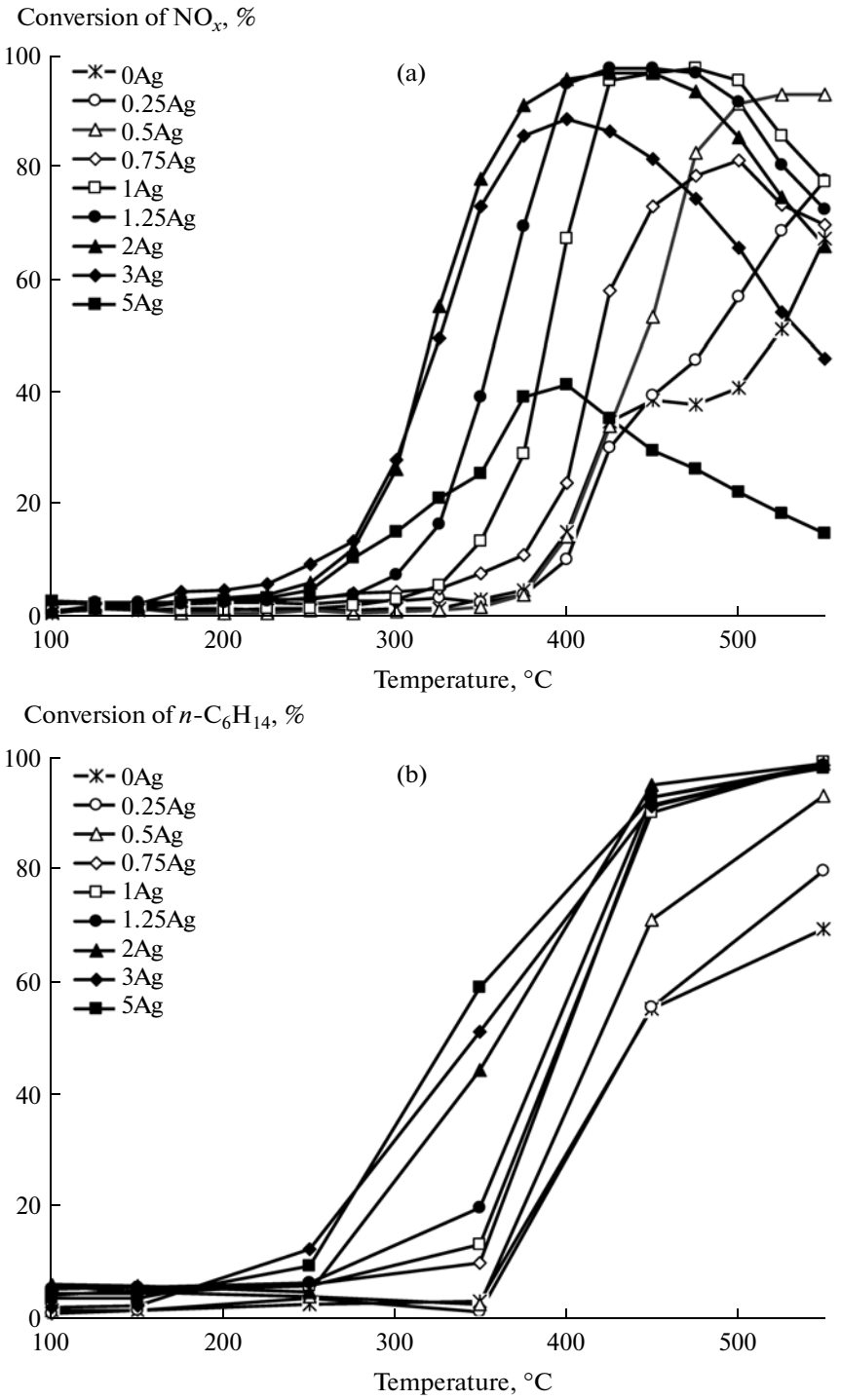

Fig. 1. The temperature dependence of the conversion of (a) nitrogen oxides and (b) *n*-hexane on Ag/Al_2O_3 samples with different Ag contents in the absence of H_2. Reaction conditions: 300 ppm of NO, 7.5% O_2, 10% CO_2, and 300 ppm of n-C_6H_{14} in N_2; GHSV = 60000 h^{-1}. The samples are specified in the table.

X-ray photoelectron spectroscopy. The samples of silver catalysts were studied on an SPECS electron spectrometer with the use of nonmonochromatic MgK_α radiation. The energy scale of the spectrometer was calibrated against the Au $4f_{7/2}$ (84.0 eV) and Cu $2p_{3/2}$ (932.7 eV) lines. The samples, ground in an agate mortar, were placed on double-sided conductive 3M™ Scotch tape, which was fixed on a standard holder. The surface charge of the samples was compensated by irradiation with slow electrons. The residual gas pressure in the analytical chamber of the spectrometer did not exceed 5×10^{-7} Pa.

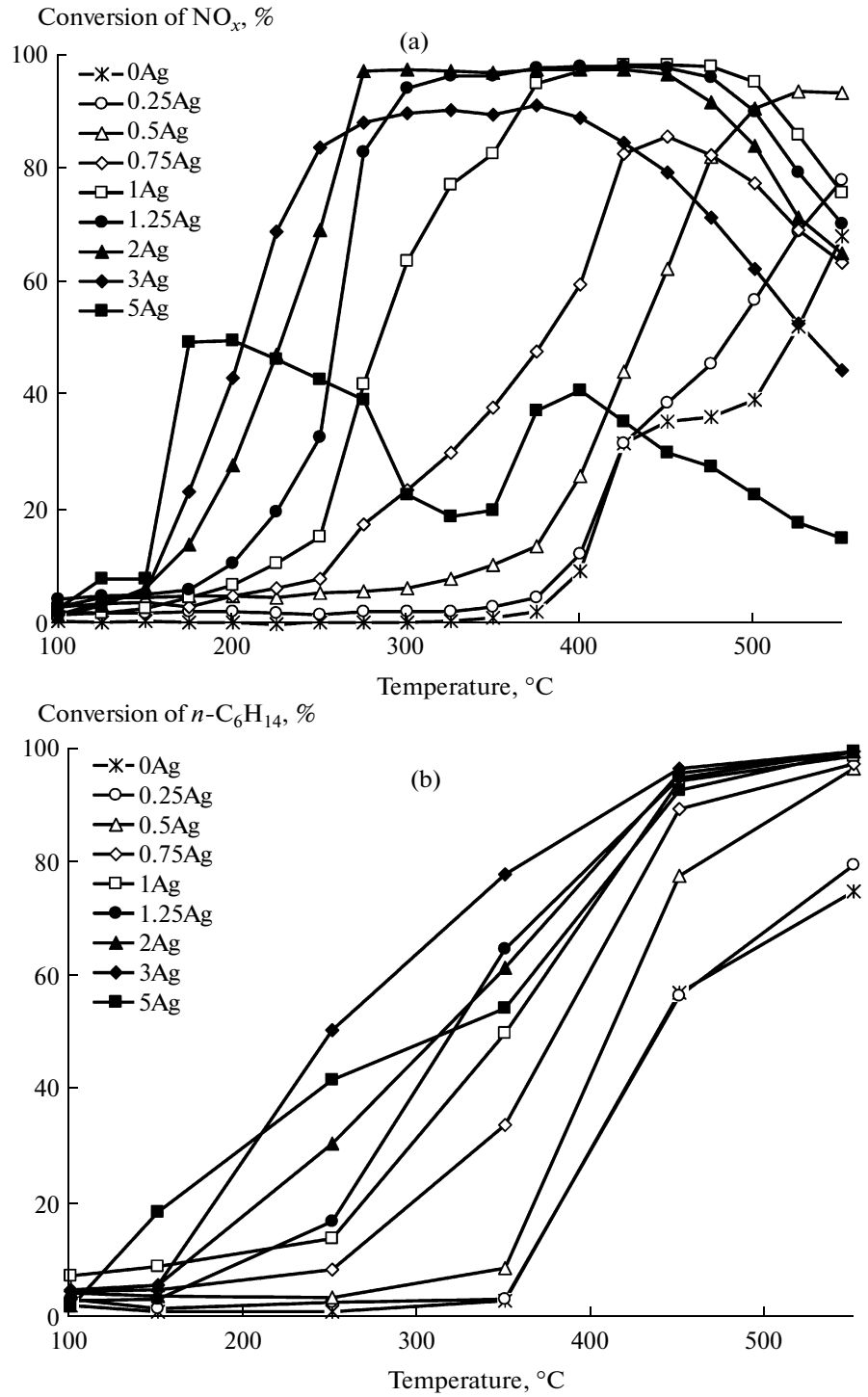

Fig. 2. The temperature dependence of the conversion of (a) nitrogen oxides and (b) *n*-hexane on Ag/Al_2O_3 samples with different Ag contents in the presence of H_2. Reaction conditions: 300 ppm of NO, 7.5% O_2, 10% CO_2, and 300 ppm of n-C_6H_{14} in N_2; GHSV = 60000 h^{-1}. The samples are specified in the table.

RESULTS AND DISCUSSION

Catalytic Activity of 0.25–5% Ag/Al_2O_3 in the SCR of NO_x with n-Hexane

SCR of NO_x with *n*-hexane in the absence of H_2. In the range of 100–450°C, the activity of the catalysts containing 0.25–0.5% Ag (Fig. 1a) was almost the same as the activity of the Al_2O_3 support [1, 26]. Above 450°C, the conversion of NO_x on these systems was higher than that on Al_2O_3, whereas the onset temperature of NO_x reduction process remained constant (375°C).

The introduction of 0.75–2% Ag into Al_2O_3 caused an increase in the catalyst activity, as was evidenced by a shift of the NO_x conversion curves towards lower temperatures by approximately 100°C. The plot of the temperature dependence of the NO_x conversion exhibits a broad plateau, which corresponds to 100% NO_x conversion, at 425–500°C on 1% Ag/Al_2O_3 or at 400–475°C on the catalysts containing 1.25–2% Ag.

A further decrease in the onset temperature of the of reaction did not occur on the samples containing 3–5% Ag. Furthermore, the conversion of NO_x on the 3% Ag/Al_2O_3 catalyst, after passing through a maximum at 400°C, sharply decreased with a further increase in the temperature. As a result, the plateau of the total NO_x conversion, which was observed for 1–2% Ag/Al_2O_3, disappeared. This tendency became even more pronounced with an increase in the concentration of Ag to 5%. On this catalyst, the conversion of NO_x was no higher than 45%.

Thus, the samples with Ag concentrations of 1–2%, which are likely the optimum concentrations for this reaction under the given conditions, exhibited the greatest activity in the SCR of NO_x with *n*-hexane in the absence of H_2. On these catalysts, the complete removal of NO_x was observed in the temperature range of 425–475°C. The decrease in the conversion of NO_x in the temperature range above 475°C is explained by the disappearance of *n*-hexane from the gas phase through the reaction of nonselective oxidation (Fig. 1b).

As the concentration of Ag in the catalyst was increased to 3–5%, the conversion of NO_x also decreased in the temperature range of 375–450°C, and this decrease cannot be explained by the oxidation of *n*-C_6H_{14}, because the NO_x conversion began to decrease when a considerable amount of *n*-hexane was still present in the gas mixture. It is believed that the reason for the change in the catalyst activity with an increase in the Ag content from 2 to 3% is the low concentration of the surface intermediates that are involved in NO_x reduction [4].

SCR of NO_x with *n*-hexane in the presence of H_2. The introduction of 1000 ppm of H_2 into the reaction mixture sharply increased the rate of reduction of nitrogen oxides and shifted the conversion curves of NO_x and *n*-C_6H_{14} to lower temperatures by approximately 100°C (Fig. 2). The onset temperature of the reaction in the presence of H_2 was 150–175°C.

Note that the effect of H_2 cannot be explained by the direct reduction of nitrogen oxides with hydrogen. Previous studies showed that, in the absence of *n*-hexane, hydrogen does not reduce NO_x on the Ag/Al_2O_3 catalysts [27], which is consistent with published data [7].

The effect of hydrogen on the rate of SCR depends on the concentration of Ag in the samples. The activities of catalysts with a low Ag content (<0.75%) remained almost unchanged at 100–550°C upon the introduction of H_2, whereas the conversion of NO_x on the catalysts with a higher concentration of Ag is significantly enhanced. The effect of H_2 on the activity of catalysts with different Ag contents can be estimated by considering the graphs of the dependence of the 25% conversion temperatures of NO_x (T_{25,NO_x}) and *n*-C_6H_{14} ($T_{25,C_6H_{14}}$) on the concentration of Ag (Fig. 3). In the region of Ag concentrations of 0.25–0.5%, the influence of H_2 on the catalyst activity was insignificant, and the efficiency of H_2 is enhanced with the concentration of Ag and reached a maximum for 1–3% Ag/Al_2O_3 (a decrease in T_{25,NO_x} by ~100°C).

The same conclusion can also be drawn based on the analysis of the dependence of the 25% conversion temperature of *n*-C_6H_{14} ($T_{25,C_6H_{14}}$) on the concentration of Ag (Fig. 3b). At low Ag concentrations (<0.75%), H_2 had almost no effect on the conversion of *n*-hexane, as was indicated by the fact that the value of $T_{25,C_6H_{14}}$ remained unchanged upon the addition of hydrogen to the reaction mixture. When the Ag content was higher than 0.75%, $T_{25,C_6H_{14}}$ considerably decreased upon the introduction of 1000 ppm of H_2.

Thus, the experimental data suggest that the catalysts containing from 1 to 2% Ag possess optimum catalytic behaviour under the conditions of H_2 promotion. At lower Ag concentrations (0.25–0.75%), the catalysts were ineffective, and the influence of H_2 was not observed. For the catalysts with high Ag concentrations (3–5%), the favorable effect of the addition of H_2 is noticeable in the temperature range of 175–350°C; however, in the high-temperature range, the effectiveness of reduction sharply decreased and, simultaneously, the temperature window of the total conversion of NO_x became narrower.

It is of interest to analyze, in detail, the influence of H_2 on the catalytic behavior of the most effective samples using 2% Ag/Al_2O_3 as an example. Figure 4 compares the curves of NO_x conversion in the presence and in the absence of H_2. Upon the addition of H_2, the reaction rate increased sharply and the conversion curve shifted by ~100°C to lower temperatures. At 250°C, the rate of SCR increased by a factor of 10–13, specifically, from ~0.008 μmol g^{-1} s^{-1} (in the absence of H_2) to ~0.105 μmol g^{-1} s^{-1} (upon the introduction of 1000 ppm of H_2). Note that, at a temperature of >275°C in the presence of H_2, NO_x was completely removed from the gas phase. Above 400°C, the introduction of H_2 was unnecessary because the rate of SCR is sufficient for the 100% conversion of nitrogen oxides even in the absence of H_2 (Figs. 1, 2, 4).

Selectivity of the Ag/Al_2O_3 Catalysts

As was noted above, selectivity is an important characteristic of the SCR of NO_x. Figure 5 illustrates the variation of the selectivity of the reduction of NO_x by *n*-hexane in the temperature range of 150–550°C on the catalysts containing 2 and 3% Ag in the pres-

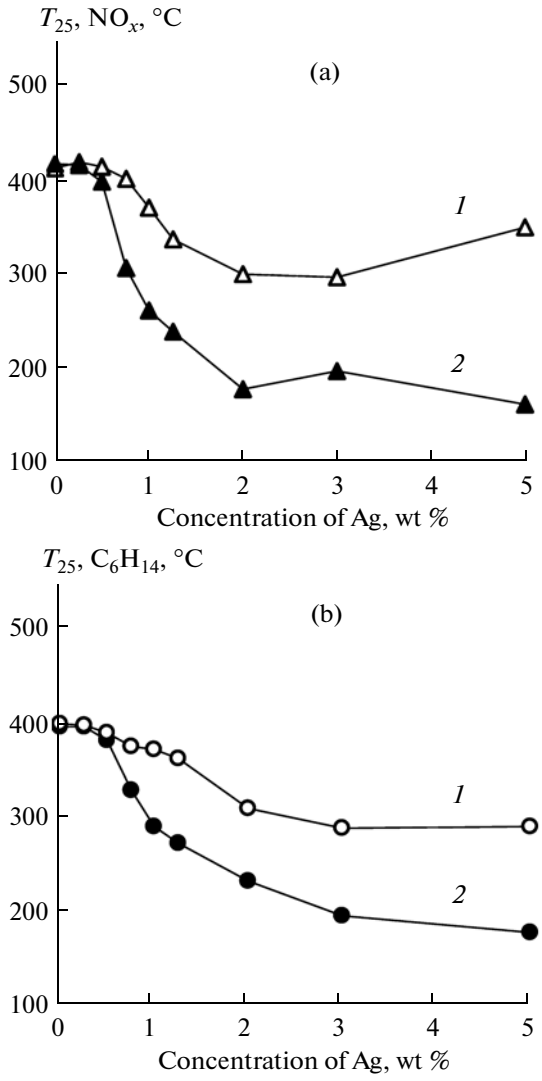

Fig. 3. Dependence of the temperatures of the 25% conversion of (a) NO_x and (b) n-C_6H_{14} on the concentration of Ag in the SCR reaction of NO_x with n-C_6H_{14} (*1*) in the absence and (*2*) in the presence of H_2. Reaction conditions: 300 ppm of NO, 7.5% O_2, 10% CO_2, 300 ppm of n-C_6H_{14}, and 0/1000 ppm of H_2 in N_2; GHSV = 60000 h^{-1}.

ence and in the absence of H_2. From the above data, we can conclude that the addition of hydrogen has almost no effect on the selectivity of the reaction. This fact is consistent with the reports that H_2 does not participate in the SCR of NO_x as a reducing agent [7, 27].

In the temperature range of 150–250°C, selectivity changed only slightly and reached a maximum value of 3 mol NO/mol n-C_6H_{14}, which indicates the high efficiency of the catalysts and the possibility of their practical use. The selectivity of reaction decreased with temperature, and it was ~1 mol NO/mol n-C_6H_{14} at 450–500°C.

The results obtained in this work and published data suggest that n-hexane is involved in the following

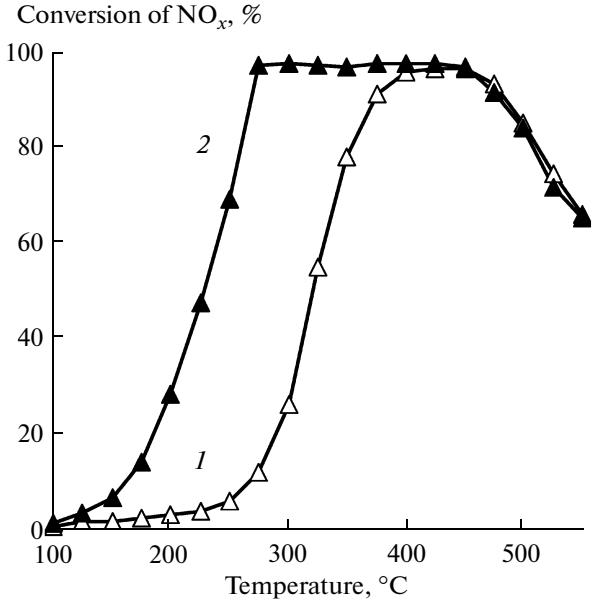

Fig. 4. Comparison between the temperature dependences of the conversion of nitrogen oxides in the SCR reaction of NO_x with n-hexane (*1*) in the absence and (*2*) in the presence of H_2 on the 2% Ag/Al_2O_3 sample. Reaction conditions: 300 ppm of NO, 7.5% O_2, 10% CO_2, 300 ppm of n-C_6H_{14}, and 0/1000 ppm of H_2 in N_2; GHSV = 60000 h^{-1}.

two parallel processes: the SCR of NO_x (reaction (I)) and nonselective oxidation by atmospheric oxygen (reaction (II)). It is likely that the decrease in the selectivity of the SCR of NO_x at temperatures higher than 250–300°C is due to the increase in the contribution of oxidation reaction (II).

$$2NO_x + C_nH_m + (n + m/4 - 2x)O_2 = N_2 + nCO_2 + m/2H_2O, \quad \text{(I)}$$

$$C_nH_m + (m/4 + n)O_2 = nCO_2 + m/2H_2O. \quad \text{(II)}$$

The selectivity of the SCR of NO_x also decreased with an increasing concentration of Ag in the catalyst. For example, in the 3% Ag/Al_2O_3 sample, the selectivity was no higher than 2 mol NO/mol n-C_6H_{14} at 250°C (Fig. 5b); that is, in this case, the contribution of the nonselective oxidation of n-hexane is higher than on the 2% Ag/Al_2O_3 catalyst.

Physicochemical Catalyst Characterization

X-ray photoelectron spectroscopy. Figure 6 shows the Ag $3d_{5/2}$ and Ag $3d_{3/2}$ XPS spectra. With increasing the concentration of Ag, the intensity of the Ag $3d_{5/2}$ line increases, but its position remains unchanged and the binding energy remains to be ~368.1 eV [25]. It should be noted that the position of the Ag 3d line is little sensitive to a change in the degree of Ag oxidation and it does not allow us to suggest the oxidation state

of particles localized on the surface of Al_2O_3 upon the variation of the Ag concentration [28].

The surface concentration of Ag determined by XPS depends linearly on the bulk concentration of silver (Fig. 7). This dependence indicates that Ag particles are small and uniformly distributed over the support surface; therefore, their overall volume is accessible for analysis by XPS.

UV spectroscopy. Figure 8 shows the UV spectra of silver catalysts with different Ag contents. The spectrum of Al_2O_3 exhibits a broad absorption band at 240 nm. According to published data, a similar absorption band, which corresponds to absorption by Ag^+ and Ag^{2+} ions, is present in the spectra of silver catalysts [15, 24, 29]. However, based on the experimental spectra, it is difficult to make quantitative conclusions on changes in the intensity of this absorption band with depending on an increase in the Ag content. This leads to an ambiguity in the interpretation of the results.

It should be noted that the introduction of Ag leads to the appearance of new absorption bands at 305 and 360 nm in the spectrum. The absorption band at 305 nm is due to the absorption of the small clusters of oxidized silver $Ag_n^{\delta+}$ [21, 24, 29, 30], which are formed on the surface of the support when the concentration of Ag increases. The appearance of the latter absorption band (360 nm) is explained by absorption caused by the silver metal clusters Ag_m^0 formed on the catalyst surface [31].

The appearance of absorption bands from small silver particles in the samples containing 0.75–2% Ag was accompanied by an increase in the rate of NO_x reduction by *n*-hexane both under the traditional conditions of this reaction and under the conditions of H_2 effect. As the concentration of Ag was further increased to 3–5%, a broad absorption band at 400 nm appeared in the spectra as a shoulder at 360 nm. According to published data, the appearance of absorption bands at wavelengths higher than 400 nm is caused by absorption by relatively large silver metal particles, which are inactive in the NO_x selective catalytic reduction [15, 24, 29].

Thus, the UV-spectroscopic data indicate that $Ag_n^{\delta+}$ and Ag_m^0 clusters predominate on the surface of samples active in the SCR of NO_x.

H_2 TPR. The TPR data are consistent with the results of UV spectroscopy, and they confirm the existence of various Ag-containing forms. In the TPR spectra (Fig. 9), it is possible to distinguish two basic regions of hydrogen uptake at 430 and 355°C.

In the spectrum of the sample with a small Ag concentration (0.75%), there is a distinct high-temperature peak of hydrogen uptake. This peak is likely due to the reduction of Ag^{2+} ions, which occur as $AgAl_2O_4$ structures, the formation of which on the catalyst surface was found by She and Flytzani-Stephanopoulos

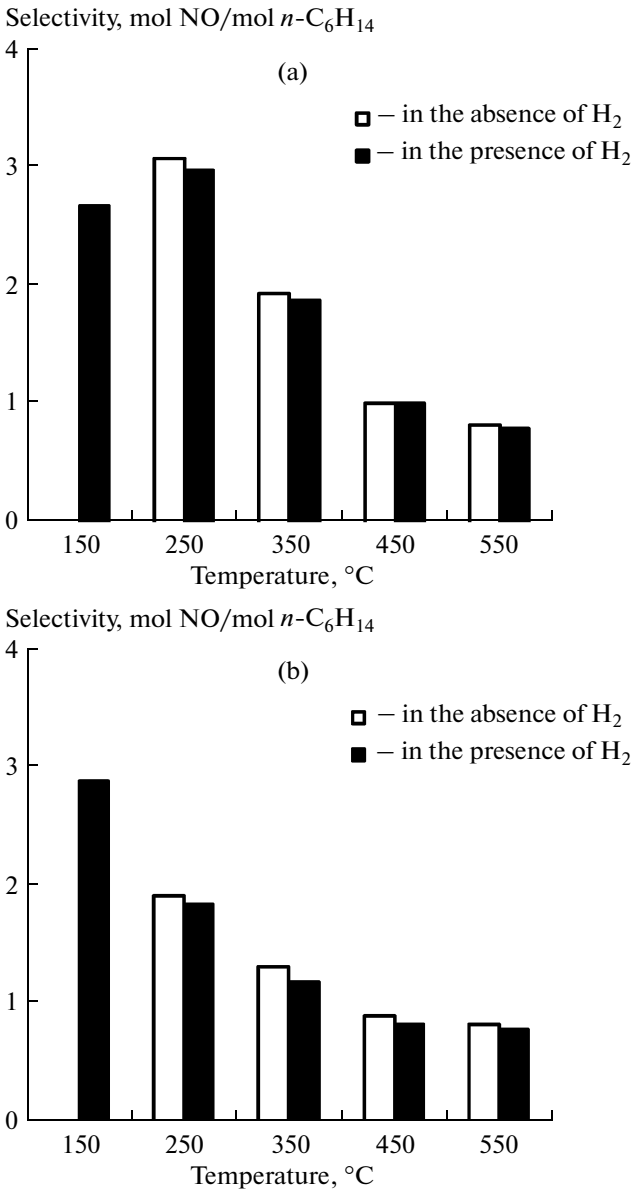

Fig. 5. The temperature dependence of the selectivity of the SCR of NO_x with *n*-hexane in the presence and in the absence of H_2 on the samples of (a) 2% Ag/Al_2O_3 and (b) 3% Ag/Al_2O_3. Reaction conditions: 300 ppm of NO, 7.5% O_2, 10% CO_2, 300 ppm of n-C_6H_{14}, and 0/1000 ppm of H_2 in N_2; GHSV = 60000 h^{-1}.

[15]. The amount of H_2 absorbed upon the TPR by a catalyst with a low Ag content is higher than the stoichiometric amount required for the reduction of Ag^+, which can also indicate that silver, at least partially, occurs in the state Ag^{2+} characteristic of aluminate structures.

The contribution from this form of silver (T_{red} = 430°C) decreases with an increasing concentration of Ag (>0.75%), and the form whose reduction occurs at 355°C becomes dominant on the catalyst surface (in this case, the peak of H_2 uptake is gradually shifted

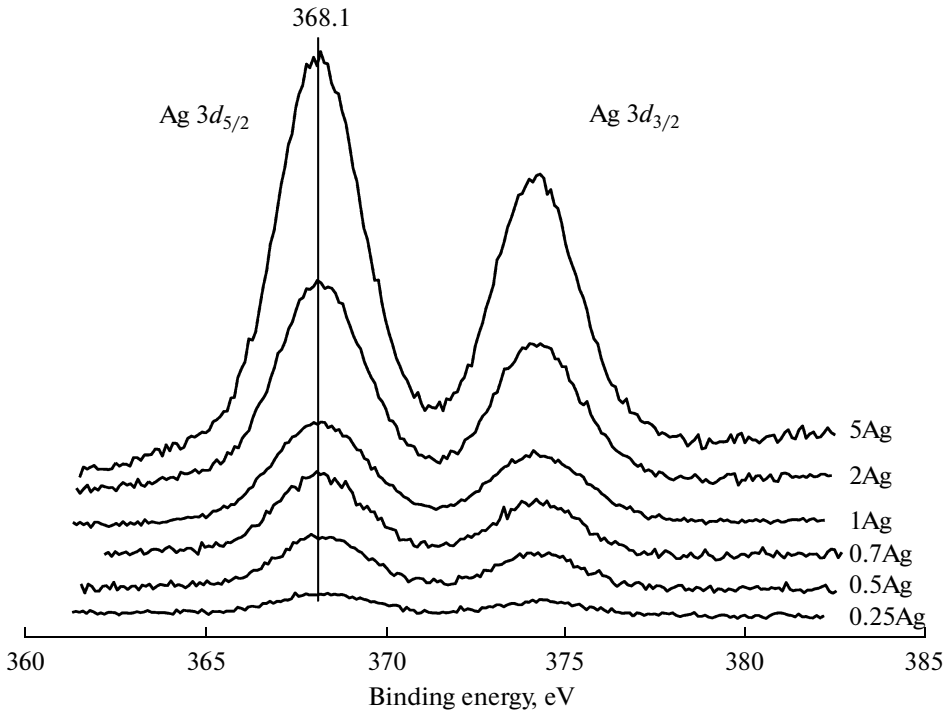

Fig. 6. XPS spectra of the Ag 3*d* line of Ag/Al_2O_3 samples with different Ag contents. The samples are specified in the table.

toward low temperatures as the Ag content is increased). Probably, the absorption of H_2 in this region is due to the reduction of small $Ag_n^{\delta+}$ clusters [32, 33], which are formed on the catalyst surface with increasing the content of silver. An increase in the size of $Ag_n^{\delta+}$ clusters and the formation of larger particles [6–8, 31, 34–36] leads to a shift the H_2 uptake peak to lower temperatures. Furthermore, with an increasing Ag content, an additional peak at ~200°C appears in the TPR curves; this peak can be ascribed to the reduction of large Ag_2O particles. It should be noted that the H_2 : Ag ratio decreased from 0.8 to 0.3 with increasing the Ag content; this fact suggests the predominance of Ag^+ and Ag^0 in the samples with high silver contents.

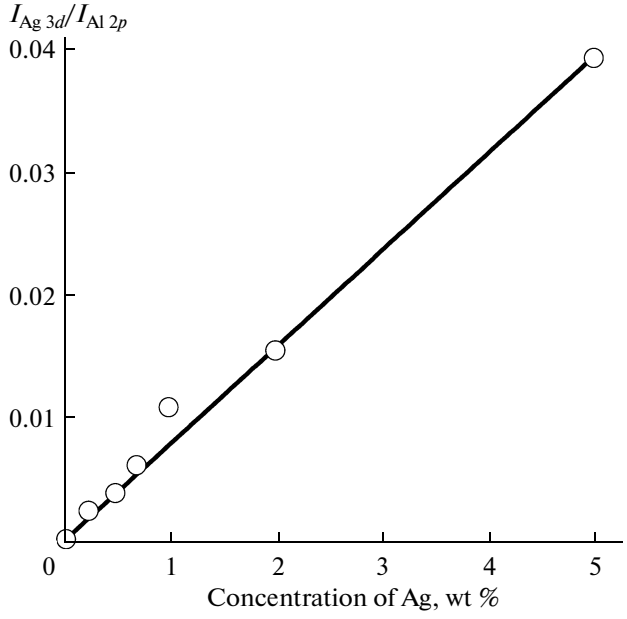

Fig. 7. Experimental intensity ratios between the Ag 3*d* and Al 2*p* signals for Ag/Al_2O_3 catalysts with different Ag contents (see table).

Thus, the comparison of the results of physicochemical studies with the data of catalytic experiments suggests that the samples containing <0.75% Ag show low activity in the SCR of NO_x by *n*-hexane. This is because a large proportion of silver is present in the ionic form Ag^+ or Ag^{2+}, probably, as the stable compound $AgAl_2O_4$, which is inactive in the SCR of NO_x even in the presence of H_2. The activity of silver catalysts containing 0.75–2% Ag is much higher; this may be due to the formation of $Ag_n^{\delta+}$ clusters. In the same interval of silver concentrations, the effect of H_2 leads to an increase in the rate of SCR and to a decrease in the reaction temperature by ~100°C (Figs. 2 and 3).

A further increase in the Ag content to 3–5% leads to the intense agglomeration of an Ag-containing phase and to the formation of the large particles of Ag_2O and Ag^0 [6–8, 30, 31, 34–36]. The experimental

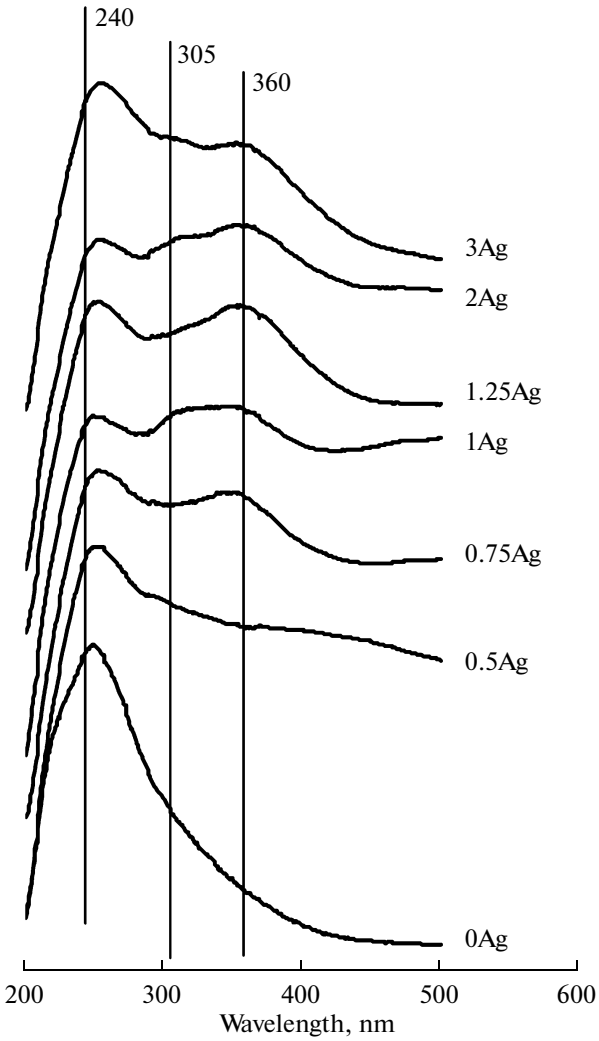

Fig. 8. UV spectra of Ag/Al_2O_3 samples with different Ag concentrations. The samples are specified in the table.

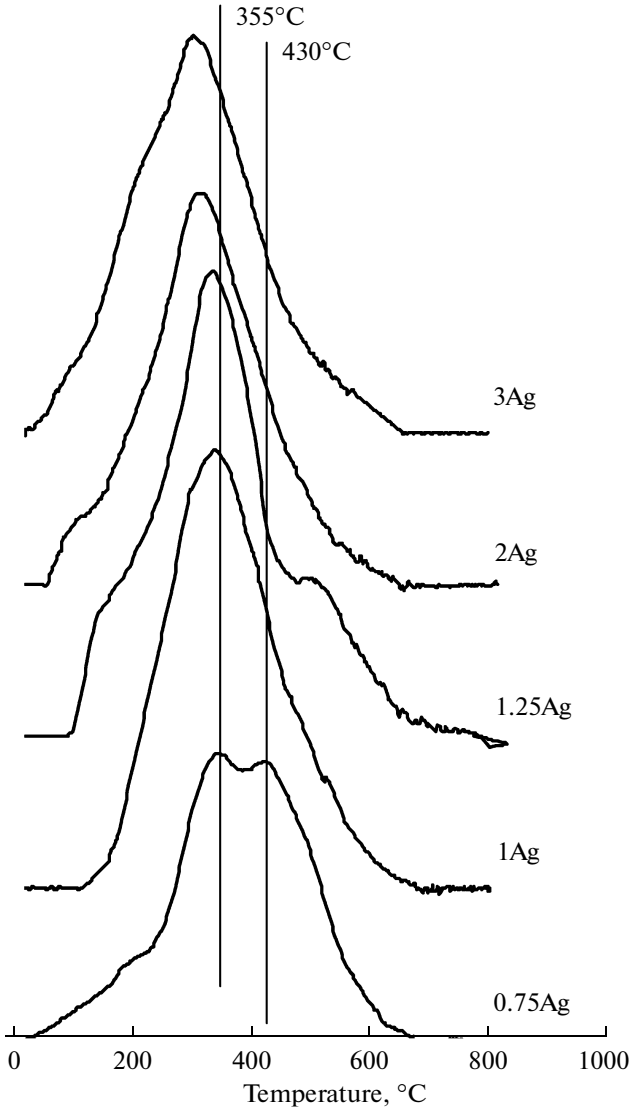

Fig. 9. TPR profiles of Ag/Al_2O_3 samples with different Ag concentrations. The samples are specified in the table.

catalytic data make it possible to conclude that the presence of such particles adversely affects the activity of catalysts in SCR. For 3% Ag/Al_2O_3, a narrowing of the region of the total conversion of NO_x was observed, whereas a decrease in the maximum degree of NO_x conversion was observed in the sample with 5% Ag/Al_2O_3. These processes can be related to the increased oxidizing activity of large Ag_2O and Ag^0 particles, which increases the contribution from the reaction of the direct oxidation of *n*-hexane (Figs. 1b and 2b) and, probably, leads to the oxidation of H_2. The last conclusion is hypothetical because the hydrogen content of the reaction products was not controlled in our experiments.

The increased oxidizing activity of the catalysts with a high Ag content causes a noticeable decrease in the reaction selectivity, which decreases to 1 mol NO/mol *n*-C_6H_{14} (250–350°C) with the concentration of Ag even in the presence of H_2.

Thus, the experimental data indicate that the use of low H_2 concentrations (1000 ppm) for the promotion of the SCR of NO_x by *n*-hexane makes it possible to considerably increase the rate of reaction and to decrease the temperature of the effective reduction of NO_x by approximately 100°C. The optimum course of the reaction in the presence of H_2 was reached with the catalysts containing 1–2% Ag, which resulted in the 100% conversion of NO_x in a wide temperature range (175–475°C) at a high GHSV (60000 h^{-1}). The selectivity of the reduction of nitrogen oxides was ~3 mol NO/mol *n*-C_6H_{14} at 250°C, and it decreased as the reaction temperature was increased to 350°C.

The study of the catalysts with the use of a set of physicochemical techniques makes it possible to conclude that small $Ag_n^{\delta+}$, clusters are the active forms of silver formed on the surface of Ag/Al_2O_3 with an opti-

mum concentration of Ag (1–2%). In the samples with lower Ag contents (<1%), the ionic forms Ag^+ and Ag^{2+}, which are inactive in SCR and sensitive to H_2 promotion, are predominant. On the surface of catalysts containing 3–5% Ag, the large particles of silver metal are formed to result in a decrease in the selectivity of SCR and also a decrease in the maximum conversion of NO_x with the retention of the effect of H_2 promotion.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant no. 10-03-01138a).

N.A. Sadokhina is grateful to Haldor Topsøe A/S for financial support in the framework of Russian Ph.D. Scholarship Programme.

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