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CATALYTIC REACTION MECHANISMS

Ammonia Formation on (Ru + Cs)/C Catalysts by the Interaction of Adsorbed Nitrogen with Hydrogen That Diffused from the Bulk of Cesium–Ruthenium Particles

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Abstract—The high-temperature α ($T_{\max}$ = 625 K) and β ($T_{\max}$ = 750 K) states of ammonia and α ($T_{\max}$ = 550–750 K), β ($T_{\max}$ = 750–900 K), and γ ($T_{\max}$ > 900 K) states of hydrogen were detected on (Ru + Cs)/C catalysts for ammonia synthesis activated under the reaction conditions (P = 30 atm; T = 650 K; the initial pressure ratio P_{N_2}/P_{H_2} = 1/3). A mechanism was proposed for the formation of ammonia as a result of the interaction of chemisorbed nitrogen with hydrogen that diffused from the bulk of cesium–ruthenium particles.

INTRODUCTION

Interest in the synthesis of ammonia from nitrogen and hydrogen on ruthenium systems has quickened in the past few years. This is primarily due to the fact that in the presence of ruthenium catalysts the reaction occurs at lower pressures than that in the case of well-known compositions based on magnetite [1, 2]. Current concepts of the mechanism of ammonia synthesis on ruthenium catalysts are mainly based on the results of kinetic studies and data on the interaction of nitrogen and hydrogen obtained with the use of physicochemical techniques at low pressures. The commonly accepted reaction mechanism includes the steps of the dissociative adsorption of nitrogen and hydrogen, the consecutive addition of hydrogen atoms to nitrogen, and the desorption of ammonia (for example, see [3, 4]).

In this work, based on the thermal desorption studies of (Ru + Cs)/C catalysts activated under reaction conditions, we proposed a new mechanism for ammonia formation at 550–800 K as a result of the interaction of chemisorbed nitrogen with hydrogen dissolved in cesium–ruthenium particles.

EXPERIMENTAL

In this study, catalysts containing 4% Ru, 13.6% Cs, and 82.4% C (series **A** and **B**) were tested. The catalysts were prepared by successively supporting ruthenium (from the carbamide complex of Ru(II)) and cesium (from a $CsNO_3$ solution) on the surface of Sibunit (S_{BET} = 320 m^2/g). Next, the samples of series **A** were treated with Ar (2 h at 623 K) and H_2 (2 h at 573 K), whereas the catalysts of series **B** were treated in the reverse sequence. The samples of series **B** exhibited a higher dispersity and a more uniform distribution of cesium and ruthenium over the support grain [5].

The synthesis of ammonia was performed in a flow reactor of stainless steel at P = 30 atm, T = 650 K, and the reactant ratio N_2/H_2 = 1/3. The activity of the catalysts was evaluated from the ammonia content (%) at the reactor output.

The samples were cooled to room temperature in the reaction atmosphere after catalytic experiments. Next, ~30 mg of the catalyst was ground and mixed in a mortar in air; a portion (2 mg) of the resulting powder was placed in a vacuum chamber for studying by temperature-programmed desorption–mass spectrometry (TPD–MS).

The experimental setup was specially designed for studying powdered samples [6]. The gas-phase analysis was performed using an MX-7304 monopole mass spectrometer with a resolving power equal to 2 M at a 50% level. The energy of ionizing electrons was 70 eV. The pressure of residual gases in the chamber was no higher than 10^{-5} Pa.

The samples were heated to 1000 K at a rate of 0.2 K/s with no pretreatment, and ~20 mass spectra were recorded over the range of m/z from 1 to 155.

To determine the quantitative composition of a gas phase, the intensity ratios between the main and secondary peaks in the mass spectra of a number of molecules were measured in advance (see the table). The values obtained are consistent with published data [7].

RESULTS AND DISCUSSION

Although the samples of series **A** and **B** had the same composition, they were significantly different in activity. The NH_3 content was ~12% on the catalysts of series **A**, whereas it was <0.1% on the samples of series **B**. A conceivable reason for this difference consists in the high dispersity of ruthenium (up to the atomic level) in the inactive catalyst [5].

The mass spectra exhibited peaks corresponding to m/z = 2, 12, 14, 15, 16, 17, 18, 28, 30, 44, 133, 149, and 150. The thermal desorption (TD) spectra of individual compounds or molecules were constructed after the determination of the current composition of a gas phase.

In our case, the TD spectra were comparatively easy to construct. First, it is clear that the set of molecules (or compounds) that can be desorbed from the surface of catalysts is limited (H_2, NH_3, N_2, $C_xH_y(OH)_z$, and Cs, as well as O_2, H_2O, CO, NO, CO_2, and CsOH, which could be formed by the interaction of the sample with the atmosphere). In this context, it is obvious that the TD spectrum for the mass m/z = 2 depends only on the desorption of H_2 (Fig. 1), whereas the TD spectra for m/z = 18, 30, 44, 133, and 149 correspond to H_2O, NO, CO_2, Cs, and CsOH (for the CsOH molecule, the main peak corresponds to the CsO fragment), respectively. Because peaks with m/z = 13, 26, 27, and 31, which are characteristic of hydrocarbons and alcohols, were absent from the mass spectra, we concluded that $C_xH_y(OH)_z$ compounds were not desorbed from the catalyst surfaces.

Because the resolving power of the mass spectrometer did not allow us to resolve signals from OH^+ and NH_3^+, as well as from NH^+ and NO^{2+}, the TD spectrum of ammonia was calculated using the following two procedures: (1) with consideration for the contribution of H_2O to the total intensity of a peak with m/z = 17 by the equation $I_{17} - k(H_2O, 17)I_{18}$, where $k(H_2O, 17)$ = 0.23 (see the table) and (2) from the relation $1/0.08(I_{15} - k(NO, 15)I_{30})$ (with consideration for the contribution of NO^{2+} to the intensity of a peak with m/z = 15). In both cases, the same results were obtained with good accuracy (5%). The TD spectra of N_2 and CO were constructed using an analogous procedure. The final verification of the TD spectra, which was performed by calculating mass spectra from them (with the use of data given in the table), demonstrated that the calculated and experimental mass spectra were in complete agreement.

The most significant differences (by one order of magnitude or more) in the TD spectra of samples from series **A** and **B** were found for NH_3 and H_2. The TD spectra of the other molecules differed only slightly.

The following three states can be recognized in the TD spectrum of hydrogen of a catalyst from series **A** (Fig. 1): α with the temperature of desorption (T_{des}) in the range 550–750 K; β with T_{des} = 780 K; and γ, which corresponds to the hydrogen desorption that began at 900 K. The amount of hydrogen desorbed from the surface of a catalyst from series **B** at temperatures lower than 900 K was smaller by approximately one order of magnitude.

Peak intensity ratios in the mass spectra of some molecules

Molecule	m/z (ntensity ratio, arb. u.)
H_2	1 (0.02), 2 (1)
NH_3	14 (0.02), 15 (0.08), 16 (0.8), 17 (1)
H_2O	16 (0.01), 17 (0.23), 18 (1)
N_2	14 (0.16), 28 (1)
CO	16 (0.1), 28 (1)
NO	14 (0.075), 15 (0.01), 16 (0.01), 30 (1)
CO_2	16 (0.09), 28 (0.1), 44 (1)

The desorption of ammonia and hydrogen (α and β states) from the surface of an active catalyst occurred within the same temperature range (cf. Figs. 1 and 2). Two states with T_{max} = 625 and 750 K can be recognized in the TD spectra of ammonia. The amount of ammonia desorbed from the surface of an inactive catalyst was smaller than that in the experiment with a sample from series **A** by at least two orders of magnitude.

Previously, it was found that hydrogen that was chemisorbed on ruthenium at pressures much lower than atmospheric pressure was desorbed at much lower temperatures, for example, as high as 400 K from Ru(11–21) and Ru(0001) [8, 9]. In the decomposition of adsorbed NH_x species, the desorption of hydrogen occurred at temperatures no higher than 500 K [10, 11]. High-temperature states of hydrogen on pure ruthenium were not detected after the adsorption at P < 1 atm. However, high-temperature hydrogen species can appear under more severe conditions. Thus, after the synthesis of ammonia on Ru(0001) at P = 2 bar, the release of hydrogen from the bulk was observed over a tempera-

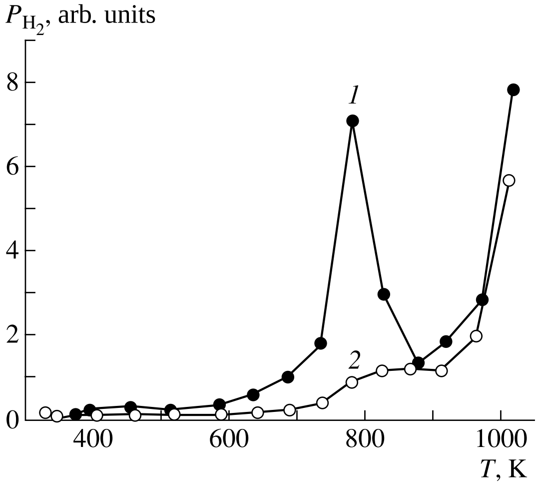

Fig. 1. TD spectra of hydrogen for (*1*) active and (*2*) inactive (Cs + Ru)/C catalysts.

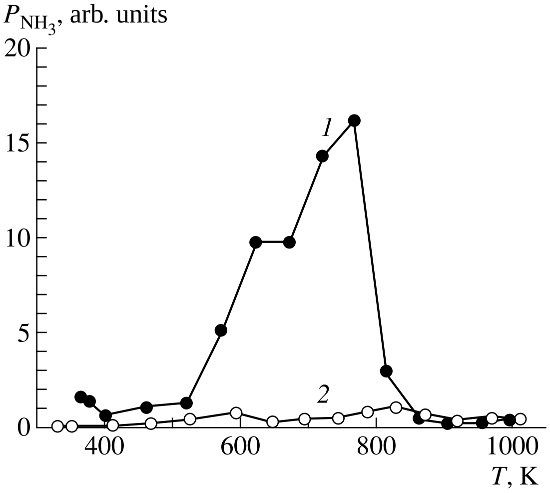

Fig. 2. TD spectra of ammonia for (*1*) active and (*2*) inactive (Cs + Ru)/C catalysts.

ture range of 600–1300 K [12]. In this case, the rate of hydrogen desorption almost linearly increased with temperature. The appearance of several states of hydrogen with T_{des} = 450, 550, and 650 K was detected upon hydrogen adsorption on the (10–10) face after nitrogen preadsorption (using stimulation with electrons from an ionization detector) [13]. It was assumed that the first state was due to the decomposition of NH^{ads}, whereas the second and third states corresponded to either the decomposition of NH_x^{ads} compounds or the stabilization with chemisorbed nitrogen. However, the latter is in contradiction to published data [14], which suggests that nitrogen destabilizes hydrogen on the Ru(0001) face. Moreover, a state of hydrogen with a desorption temperature range of 450–600 K was also observed on a Ru/MgO catalyst [15].

There is no published data on the effect of cesium on the state of hydrogen adsorbed on ruthenium. It is only known that the heat of hydrogen chemisorption on ruthenium decreased in the presence of cesium [16]. This decrease should shift peaks in the TD spectra of adsorbed hydrogen toward low temperatures.

Thus, it is improbable that the states of hydrogen detected in this work are due to its desorption from the surface. It is likely that the α and β states, which are shown in Fig. 1, correspond to hydrogen released from a near-surface region, whereas the γ state corresponds to the release from the bulk of cesium–ruthenium particles. It is of interest that the formation of the $Cs_{3-\delta}RuH_{7-\delta}$ hydride at a hydrogen pressure of 1500 bar was found recently [17]. It is likely that in our case the formation of a hydride-like Cs_xRuH_y compound rather than the dissolution of hydrogen also took place under the reaction conditions (30 atm). Structural distortions caused by the high dispersity of the active component and by the reaction atmosphere can serve to decrease the activation energy of hydrogen diffusion into the bulk of cesium–ruthenium particles. Therefore, the formation of Cs_xRuH_y can occur at lower pressures. On heating this sample under vacuum conditions, the Cs_xRuH_y hydride can undergo degradation followed by hydrogen diffusion into the near-surface region and then to the surface in accordance with the following scheme:

$$Cs_xRuH_y \longrightarrow Cs_xRuH_{y-1} + H^{dissolved},$$

$$H^{dissolved} \longleftrightarrow H^{subsurface} \longleftrightarrow H^{adsorbed}.$$

The desorption of ammonia from the surface of ruthenium metal under high-vacuum conditions was observed previously only at $T < 350$ K [18]. At higher temperatures, ammonia was decomposed with the release of hydrogen (up to 500 K) and then nitrogen at 600–900 K [11]. It is well known that the promotion of a ruthenium surface with cesium decreased the binding energy of ammonia with ruthenium [19].

In the context of the above consideration, the most reasonable explanation of the desorption of ammonia observed at high temperatures consists in its formation by the interaction of adsorbed nitrogen with hydrogen diffused from the bulk. At high coverages with nitrogen molecules (T = 500–600 K), all hydrogen was bound with nitrogen, and only the desorption of ammonia was observed. As the surface coverage with nitrogen decreases, the associative desorption of hydrogen occurs with greater probability; this manifests itself initially in a smooth increase in the rate of hydrogen desorption (up to T = 700 K) and then in a dramatic increase in this rate (T = 700–800 K), when the surface concentration of nitrogen is low. At a higher temperature (T = 900–1000 K), only the desorption of hydrogen released from the bulk of particles is observed.

The detailed mechanism of ammonia formation in the case under consideration remains unclear. The consecutive addition of hydrogen atoms to NH_x^{ads} (x = 0, 1, or 2) seems improbable because, as mentioned above, both the decomposition of NH_x^{ads} species and the associative desorption of adsorbed hydrogen rapidly occur at $T > 500$ K [8, 11, 20]. Therefore, one of the conceivable explanations of NH_3 formation at $T > 500$ K may consist in the interaction of adsorbed nitrogen or amino groups with one or more hydrogen atoms simultaneously, which occur in the near-surface region or are inserted into the surface: $NH_x^{ads} + yH^{subsurface} \longrightarrow NH_{x+y}^{ads}$ (y, $x + y$ = 1, 2, 3). The defect surface of active particles and great amounts of near-surface hydrogen facilitate this process by eliminating structural limitations characteristic of regular surfaces.

The proposed mechanism of ammonia synthesis on (Cs + Ru)/C catalysts can be used for explaining differences in the activity of the catalysts of series **A** and **B**. The high dispersity of Ru particles in the samples of series **B** prevents the formation of a sufficient amount of dissolved hydrogen to result in a dramatic decrease in the catalytic activity.

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