

MECHANISMS OF CATALYTIC REACTIONS

On the Surface Steps of a Heterogeneous Catalytic Reaction

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Abstract—Based on a study of the properties of intermediate complexes in the reactions of low-temperature ammonia oxidation and nitrogen oxide reduction in the presence and absence of oxygen on various catalysts, it was hypothesized that the sequence of steps in the formation of reaction products on chemically different catalysts can be the same if the initial adsorption forms of reactants are identical. In this case, variations in catalysts or reaction conditions affect the ratio between reaction rates.

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INTRODUCTION

The mechanism of a heterogeneous catalytic reaction is usually considered to mean a sequence of steps; in each particular step, intermediate complexes (intermediates) are formed and consumed [1]. Advances in both the theory and practice of heterogeneous catalysis are based on the knowledge of a detailed catalytic reaction mechanism.

Data on the structure and reactivity of intermediates are required for revealing the detailed mechanism of a catalytic reaction. IR spectroscopy is a suitable technique for obtaining this information.

By now, a great body of experimental data on the properties of surface complexes has been accumulated and the roles of these complexes in various reactions have been hypothesized [2–4]. However, a test is required in order to determine the true role of surface complexes in catalytic conversions. In this paper, a comparison between the rates of surface compound consumption and product formation is proposed as

such a test [5, 6]. If these rates are equal, it is believed that an identified surface compound is an intermediate in the test reaction.

The rates were determined based on spectrokinetic measurements, in which the spectra of surface compounds and the rates of formation of reaction products were measured simultaneously. After the identification of absorption bands in the IR spectra and the quantitative treatment of spectroscopic data (determination of the concentrations and the rates of conversion of surface compounds), the rates of reaction and conversion of surface compounds were compared quantitatively.

Figure 1 shows a schematic diagram of the spectrokinetic measurements. The main unit of this diagram is a spectroscopic cell, which simultaneously serves as a catalytic reactor [7, 8]. The main special features of this cell are the small volume and the absence of cold parts. The reaction mixture was analyzed before and after the reactor cell. The spectrokinetic measurements can be performed under steady-state and non-steady-state conditions.

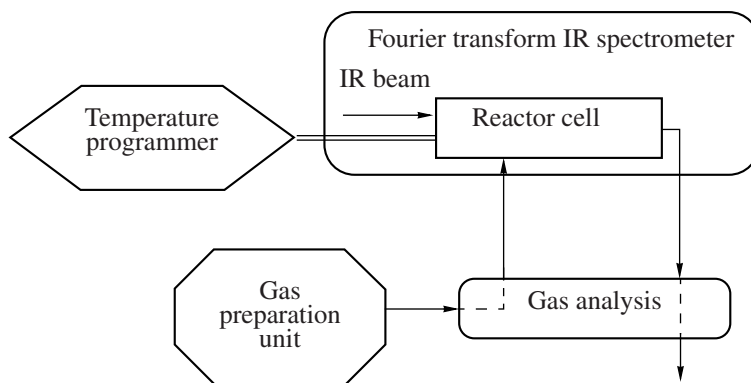


Fig. 1. Schematic diagram of the setup for spectrokinetic measurements.

An example of the quantitative comparison of the rate of reaction is calculated based on spectroscopic measurements with the rate measured experimentally under conditions of NO reduction with propane in an excess of oxygen on Cu/ZSM-5 [8]. Under reaction conditions, an absorption band at 1630 cm^{-1} was detected in the transmission spectra. According to published data [9], this absorption band was attributed to antisymmetric vibrations in the Cu–O–N=O complex. On heating the sample under thermal desorption conditions with the analysis of the amount of released NO_x molecules, the absorptivity (ϵ) was determined to be equal to $3.4 \times 10^{-18}\text{ cm}^2/\text{molecule}$.

Under reaction conditions at 300°C , the absorbance (D) of a band at 1630 cm^{-1} was equal to 0.05. By this is meant that $N_{\text{NO}_x} = DS/\epsilon = 3 \times 10^{16}$ complexes occurred on the sample surface. If NO_x is converted through this complex, the rate of reaction is $w = kN_{\text{NO}_x} = 1.8 \times 10^{17}\text{ molecule/min}$.

The value of k was determined from data in Fig. 2. Curve 1 characterizes absorbance changes at the absorption band of the nitrite complex with time upon replacing a reaction mixture flow with a flow containing propane. This procedure was oriented to terminate the formation of the nitrite complex in order to measure the rate of its consumption. The treatment of curve 1 in the coordinates of a first-order equation gave $k = 6\text{ min}^{-1}$ (see straight line 2).

The experimentally measured rate of NO_x conversion on this sample was $w = 1.9 \times 10^{17}\text{ molecule/min}$. A satisfactory agreement between the rates demonstrates that the observed complex is an intermediate in the reduction of NO_x with propane.

The above example shows that the spectrokinetic method can be successfully applied to studying the surface steps of heterogeneous catalytic reactions.

The starting reagent for subsequent reactions results from the adsorption of molecules on catalyst surfaces. The same surface complexes (the same reagents) can be formed on different catalysts. In this case, the reaction occurs by the same mechanism on these catalysts. However, if chemically different reagents are formed upon the adsorption of the same molecules on a group of catalysts, different reactions occur on these catalysts. To test this hypothesis, the spectrokinetic method was applied to study the same reaction on a wide range of catalysts.

Low-Temperature Ammonia Oxidation

The low-temperature catalytic oxidation of ammonia to nitrogen is an important process for decreasing the concentration of ammonia in industrial waste gases. Reaction intermediates in ammonia oxidation [10] were studied on oxide catalysts characterized by Lewis (Cr_2O_3 , Fe_2O_3 , and ZnO) or Brönsted acidity (Cr_2O_3 and MoO_3) and on bulk metals (Pt and Fe) [11].

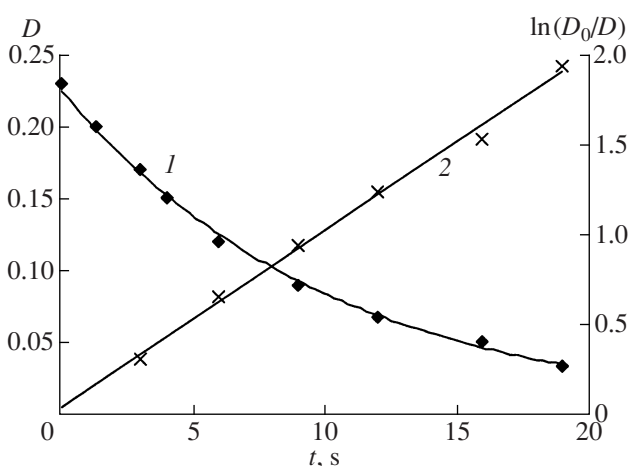


Fig. 2. (1) The time dependence of absorbance at 1630 cm^{-1} after the replacement of a flow of $\text{NO} + \text{O}_2$ with a flow of $\text{C}_3\text{H}_8 + \text{O}_2$ and (2) the result of its treatment in the coordinates of a first-order equation.

With the use of steady-state and non-steady-state spectrokinetic measurements based on transmission and diffuse-reflectance IR spectroscopy, it was found that NH_3ads and $\text{N}_2\text{O}^{\delta-}$ are reaction intermediates on ZnO and Fe_2O_3 and NH_3ads , $\text{N}_2\text{O}^{\delta+}$, and NH_2ads are reaction intermediates on Cr_2O_3 .

Assuming that all of the detected intermediates participate in the reaction, the following reaction scheme can be proposed to describe the low-temperature oxidation of ammonia on the test metal oxides:

- (1) $\text{NH}_{3\text{gas}} + \text{Z} \rightarrow \text{NH}_3\text{Z}$
(ZnO , Cr_2O_3 , Fe_2O_3 — 1620 cm^{-1}),
- (2) $\text{NH}_3\text{Z} \rightarrow \text{NH}_{3\text{gas}} + \text{Z}$,
- (3) $\text{O}_2 + \text{Z} \rightarrow \text{O}_2\text{Z}$,
- (4) $\text{O}_2\text{Z} \rightarrow \text{O}_2 + \text{Z}$,
- (5) $\text{O}_2\text{Z} + \text{Z} \rightarrow 2\text{OZ}$ (Cr_2O_3 — $1010, 990\text{ cm}^{-1}$),
- (6) $\text{NH}_3\text{Z} + \text{OZ} \rightarrow \text{NH}_2\text{Z} + \text{OHZ}$
(Cr_2O_3 — 1560 cm^{-1}),
- (7) $2\text{NH}_2\text{Z} \rightarrow \text{N}_2\text{H}_4\text{Z} + \text{Z}$,
- (8) $\text{N}_2\text{H}_4\text{Z} + \text{O}_2\text{Z} \rightarrow \text{N}_{2\text{gas}} + 2\text{H}_2\text{O} + 2\text{Z}$,
- (9) $\text{NH}_2\text{Z} + \text{O}_2\text{Z} \rightarrow \text{NOZ} + \text{H}_2\text{O} + \text{Z}$
(Cr_2O_3 — 2080 cm^{-1}),
- (10) $\text{NOZ} + \text{OZ} \rightarrow \text{NO}_2\text{Z} + \text{Z}$,
- (11) $\text{NH}_2\text{Z} + \text{NO}_2\text{Z} \rightarrow \text{N}_2\text{OZ} + \text{Z}$
(ZnO , Fe_2O_3 — 2200 cm^{-1}),
- (12) $\text{N}_2\text{OZ} \rightarrow \text{N}_2\text{O}_{\text{gas}} + \text{Z}$,
- (13) $\text{OHZ} + \text{OHZ} \rightarrow \text{H}_2\text{O} + \text{OZ} + \text{Z}$.

Here, Z is a free site of the oxide surface; oxides on which the given surface compounds were observed experimentally are specified in parentheses.

Based on the above reaction scheme, product concentrations and surface coverages with intermediate compounds at various reaction mixture compositions were calculated. The following reaction constants

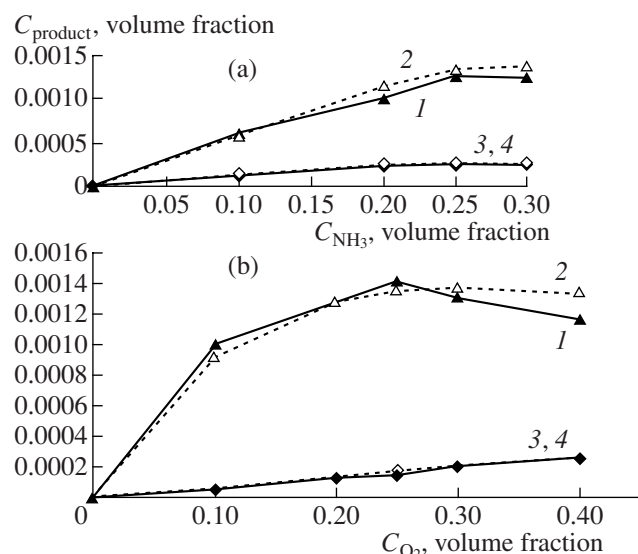


Fig. 3. Dependence of (solid line) experimental and (dashed line) calculated concentrations of the reaction products (1, 2) N_2 and (3, 4) N_2O for Fe_2O_3 on the concentrations of (a) ammonia and (b) oxygen in the reaction mixture.

obtained from non-steady-state spectrokinetic measurements were used as reference values: k_{12} (0.012 s^{-1} on ZnO and 0.020 s^{-1} on Fe_2O_3), k_6 ($1 \times 10^{-3} \text{ s}^{-1}$), and k_{10} ($2 \times 10^{-3} \text{ s}^{-1}$) on Cr_2O_3 (the dimensions of constants depend on the fact that surface coverages are expressed as monolayer fractions, and reagent and product concentrations in the gas phase are expressed in volume fractions, that is, dimensionless units).

Figure 3 shows the dependence of reaction product concentrations (both experimentally measured and calculated using the reaction scheme proposed) on the concentrations of NH_3 and O_2 . Figure 4 compares the experimental and calculated surface coverages and their changes in the course of reaction on ZnO , Cr_2O_3 , and Fe_2O_3 after the termination of ammonia supply to the reaction mixture for the oxides examined. With consideration for the assumptions made in the reaction scheme, the calculated and experimental functions are in good agreement.

The set of the above facts suggests that the reaction mechanism is the same on the test oxides. Note that the adsorption species of ammonia and oxygen on these oxides are the same. In this context, it is believed that the same mechanism of the given reaction occurs in the presence of catalysts on which the initial adsorption species of reactants are the same.

The results of spectrokinetic measurements on Lewis acidic oxides were discussed above. The NH_4^+ surface complex is formed upon ammonia adsorption on oxides with Brönsted acidity (MoO_3 and Cr_2O_3). The spectrokinetic measurements demonstrated that this complex is an intermediate in the formation of N_2O

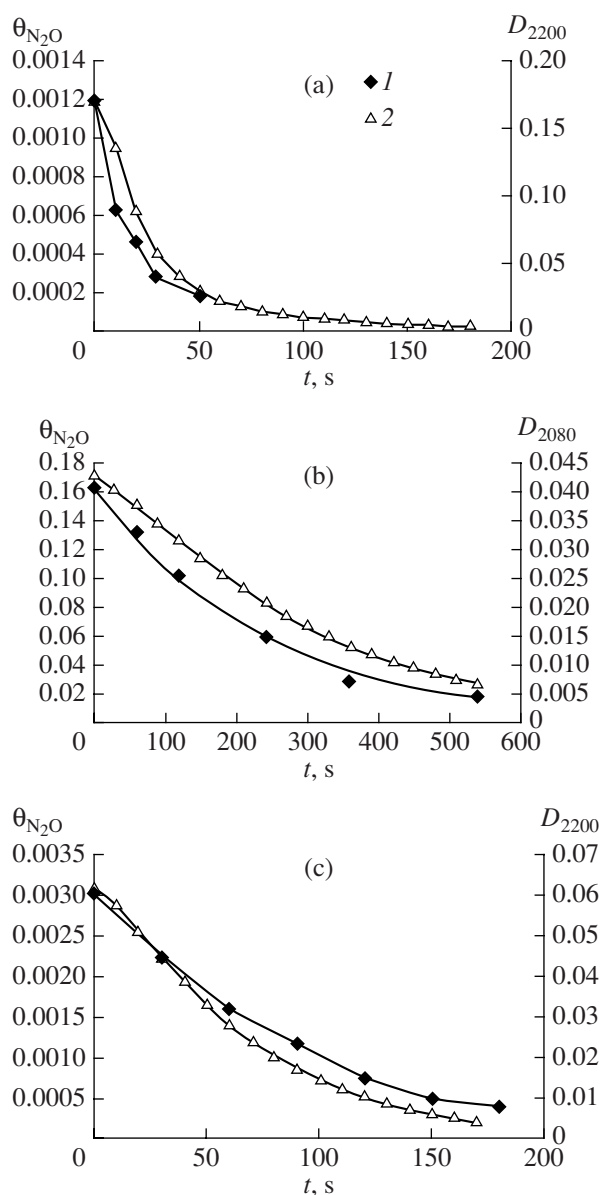


Fig. 4. (1) Experimental and (2) calculated curves illustrating the decline of absorption at (a) 2200 cm^{-1} for ZnO , (b) 2080 cm^{-1} for Cr_2O_3 , and (c) 2200 cm^{-1} for Fe_2O_3 upon ammonia shutoff.

and N_2 . Consequently, the mechanism of ammonia oxidation on these samples is the same. At the same time, it is fundamentally different from the above mechanism for Lewis acidic oxides. The results given provide support for the above hypothesis.

The oxidation of ammonia on bulk metals [11] is another example that supports our hypothesis. According to in situ emission IR-spectroscopic data, the surface NH_2 complex is the form of methane activation in this case and nitrogen oxide was detected in the reaction products.

Interaction of CO and NO

This process is important from the standpoint of gasoline vehicle emission control. The main catalysts are supported platinum group metals. In this context, the process was studied on Pt, Pd, Rh, Ru, and, for comparison, Cu⁰ supported on aluminum oxide. Under the reaction conditions, isocyanate and carbonate complexes were identified as intermediates on catalyst surfaces. In addition, carbonyl complexes were observed at relatively low temperatures, whereas nitrosyl complexes were detected at relatively high concentrations of NO. Krylov and Matyshak [12], who performed a spectrokinetic study with wide variations in the reaction atmosphere composition and temperature, found that the isocyanate complex is an intermediate in the formation of nitrogen. The NCO complex is formed by the interaction of adsorbed the nitrogen atom and CO molecule; it decomposes in a reaction with an adsorbed NO molecule. With consideration for the above, the following mechanism was proposed for the interaction between CO and NO:

- (1) $\text{CO} + [\text{M}] \rightleftharpoons [\text{M}-\text{CO}]$,
- (2) $\text{NO} + [\text{M}] \rightleftharpoons [\text{M}-\text{NO}]$,
- (3) $[\text{M}] + [\text{M}-\text{NO}] \rightarrow [\text{M}-\text{N}] + [\text{M}-\text{O}]$,
- (4) $[\text{M}-\text{N}] + [\text{M}-\text{CO}] \rightarrow [\text{M}-\text{NCO}] + [\text{M}]$,
- (5) $[\text{M}-\text{NCO}] + [\text{M}-\text{NO}] \rightarrow [\text{M}-\text{CO}_2] + \text{N}_2 + [\text{M}]$,
- (6) $[\text{M}-\text{CO}] + [\text{M}-\text{O}] \rightarrow [\text{M}-\text{CO}_2] + [\text{M}]$,
- (7) $[\text{M}-\text{CO}_2] \rightarrow [\text{M}] + \text{CO}_2$,
- (8) $[\text{M}-\text{N}] + [\text{M}-\text{NO}] \rightarrow \text{N}_2\text{O} + 2[\text{M}]$,
- (9) $\text{O}_2 + 2[\text{M}] \rightarrow 2[\text{M}-\text{O}]$.

Based on this mechanism, the dependence of the rate of reaction and selectivity on the reaction atmosphere composition was quantitatively described for all of the test catalysts (with various sets of constants). Note that the initial adsorption states of reactants in this process were the same for the test catalysts: the reaction mechanism was the same.

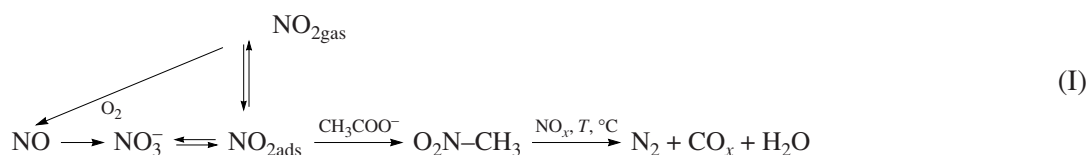
Matyshak et al. [13, 14] studied this reaction on bulk copper–cobalt spinel and copper–cobalt spinel and copper oxide supported on aluminum oxide and found that

carbon monoxide and nitrogen oxide were activated as carbonyl and nitrite complexes, respectively. A reaction between them resulted in the formation of N₂O and CO₂. By this is meant that both the form of reactant activation and the mechanism of the reaction changed.

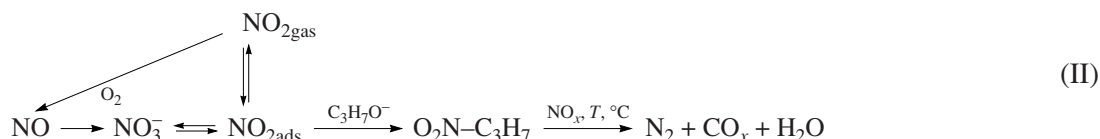
Reduction of Nitrogen Oxides with Hydrocarbons

The most interesting data were obtained in a study of the selective catalytic reduction of nitrogen oxides with hydrocarbons (HC-SCR of NO_x) in the presence of oxygen. This reaction has received much attention in the literature because of the necessity of diesel vehicle emission control. The HC-SCR of NO_x occurs most effectively on oxide catalysts [15–18]; this is likely due to the fact that the presence of oxygen facilitates the activation of NO_x on these catalysts with the formation of nitrate complexes rather than prevents this activation (this is characteristic of supported metals).

Spectrokinetic studies [19–31] allowed us to demonstrate that nitrate complexes [20–28] are key reaction intermediates in the HC-SCR of NO_x on various catalysts—copper- and cobalt-substituted zeolites with the ZSM-5 structure; various modifications of zirconium dioxide; pillared clays, in which nanosized ZrO₂ particles are fixed between the aluminosilicate layers of natural montmorillonite clays (both pure pillared clays and clays with supported active components: copper or cobalt cations, in particular, promoted with platinum or silver); and on nickel–chromium oxide, iron–chromium oxide, and copper–zinc–alumina systems (schemes (I), (II)). The next step is the interaction of NO₃[−] with a hydrocarbon with the formation of nitroorganic complexes [29–31]. Note that the structure of the nitroorganic complexes depends on the form of hydrocarbon activation. In particular, the interaction of a mixture of propylene and oxygen with the surface of bulk ZrO₂ results in the formation of only an acetate complex. Finally, the acetate and the monodentate nitrate complexes form a surface complex structurally similar to the adsorbed nitromethane (scheme (I)):



The isopropoxide complex is the main form of propylene activation on the ZrO₂ pillars of pillared clay. In this case, the isopropoxide and nitrate complexes form a complex structurally similar to the adsorbed dinitropropane (scheme (II)):



The dinitropropane complex is consumed in the interaction with surface NO_2 complexes formed by the decomposition of surface nitrates.

The set of the above data demonstrates that the initial adsorption state of reactants is responsible for the sequence of steps in the HC-SCR of NO_x : if NO and a hydrocarbon form nitrate and acetate, respectively, upon activation, the reaction proceeds through the nitromethane complex; if NO forms nitrate upon activation and a hydrocarbon forms isopropoxide, the nitropropane complex is an intermediate. This statement is true for all of the test systems.

The above facts fall within the framework of the hypothesis that the mechanism of the given reaction as a sequence of intermediate transformations on a set of catalysts is retained if the initial adsorption forms of reactants on this set are the same. Indirect evidence for this hypothesis can be found in the literature. In particular, Margolis [32], who studied propylene oxidation to acrolein on oxide catalysts, found that the mild oxidation reaction of propylene to acrolein occurs if a π complex of propylene is formed upon propylene adsorption, whereas the deep oxidation reaction of propylene occurs on the formation of a σ complex of propylene. Propylene activation as isopropoxide leads to the formation of acetone.

The methanol synthesis reaction can also be used as an example in order to support a one-to-one correspondence between the reaction mechanism and the adsorption forms of reactants. According to the concepts developed by Rozovskii [33], the synthesis of methanol proceeds solely through CO_2 rather than CO.

It is likely that the occurrence of a compensation effect [1] can be explained only in the case that the reaction mechanism is the same on various catalysts (i.e., only in the case that the measurements refer to a reaction step of the same nature on different catalysts).

In conclusion, note that the generalization of the above experimental data, which were obtained in a limited range of catalytic reactions, leads to a hypothesis the main idea of which consists in an unchanged mechanism of a particular reaction on various catalysts if the initial adsorption forms of reactants are the same on these catalysts. This hypothesis is likely not a general rule; however, it can be helpful in the discrimination of mechanisms: the detection of similar adsorption types or similar primary complexes on all catalysts allows one to consider the previously proposed mechanism as a first approximation (as a first step).

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