PHYSICOCHEMICAL PRINCIPLES OF ECOLOGICAL CATALYSIS OF GAS-PHASE REACTIONS

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In this article we summarize and correlate results obtained in numerous studies of heterogeneous catalytic gas-phase reactions with low reactant concentrations — mostly studies performed under the direction of the author at the L. V. Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of the Ukraine. Physicochemical principles are defined for the catalysis of such reactions in the presence of solid catalysts. Examples are cited to illustrate the use of these relationships in developing effective catalysts and processes of ecological catalysis, particularly for catalytic treatment of gas emissions and the development of essentially zero-waste technologies in resource-conserving and energy-efficient versions.

Catalysis, particularly catalysis of gas-phase reactions, is the method most widely used to carry out chemical conversions of substances. In the practical application of catalysis, an important area is commercial catalysis, used to obtain extremely important products in the chemical, petrochemical, petroleum refining, and other industries. Catalytic processes are especially prominent in the nitrogen industry [1]. Another important application of catalysis is the catalytic treatment of industrial gases to eliminate harmful impurities by converting them to innocuous products [2, 3]. In view of these extensive applications, we may view catalysis as the scientific foundation of chemical technology.

Chemical methods, including catalytic methods, are extremely important in solving the most critical problems of protecting the environment against highly toxic pollutants [4-6]. With this in mind, in 1980 we defined a new direction in the practical utilization of catalysis: ecological catalysis [7, 8]. This branch of the science of catalysis is concerned with the relationships in catalytic conversion reactions that can be used to solve technological problems of environmental protection. Catalytic methods that can be classed as ecological catalysis are used in wastewater treatment and also in the development of essentially zero-waste catalytic processes. In creating low-waste and zero-waste technologies, an important factor is the development and use of highly selective catalysts to increase the yields of the desired products and reduce the amount of waste; another important aspect is the development of multifunctional catalysts in the interest of simplification and intensification of commercial technologies. Much of the work in the field of ecological catalysis has been devoted to investigation of heterogeneous catalytic processes for the treatment of gas emissions to eliminate the principal atmospheric pollutants (carbon monoxide, organic and chlorine-containing substances, sulfur dioxide, carbon disulfide, ozone, and others) by converting them to innocuous products or to substances that can be easily removed by other methods. In this light, we can consider that the scientific aspects of ecological catalysis are the theoretical foundation of environmental protection technology.

The problems that ecological catalysis is required to solve are basically different from those of commercial product-oriented catalysis. Correspondingly, the processes used in these two fields of catalysis are also quite different. In commercial catalysis, many different reactions are applied, including both redox and acid–base types. Ecological catalysis, in contrast, employs only a limited group of conversions of highly toxic substances. These are mainly gas-phase reactions: oxidation by oxygen or sometimes by ozone (for example, in the treatment of air to eliminate sulfur dioxide [9, 10] or carbon disulfide [11, 13]); or, less frequently, reduction reactions (for example, the reduction of nitrogen oxides by hydrogen [14], by carbon monoxide [15, 16], or by methane [17], and the reduction of sulfur dioxide by carbon monoxide [18, 19]); or, much less frequently, decomposition reactions (in particular, the decomposition of ozone [20, 21]). These reactions are based on
conversions of substances to either harmless or valuable products. Harmless products are obtained in the oxidation of organic substances or carbon monoxide, in the reduction of nitrogen oxides, and in the decomposition of ozone; valuable products are obtained in the oxidation of chlorine-containing compounds to form chlorine, in the oxidation of sulfur dioxide to sulfur trioxide for the production of sulfuric acid, in the reduction of sulfur dioxide to elemental sulfur, and so on.

Processes of ecological catalysis are based on information on the reaction kinetics and mechanism and are subject to the general relationships of heterogeneous catalysis [22]. However, ecological catalysis is characterized by certain specific features that have been established, in particular, in studies of processes for the treatment of industrial gases [2, 23] and gaseous emissions. The unique features of processes of ecological catalysis in the treatment of gaseous emissions are related mainly to the low concentrations of toxic substances that must be eliminated from the gas mixture; with these low concentrations, the catalyst surface coverage by these substances will be very low. Processes of ecological catalysis, the same as all heterogeneous catalytic reactions, may proceed in any or all kinetic regimes — in the kinetic and diffusion region — and in some cases in the heterogeneous/homogeneous regime. The distinctive feature of processes of ecological catalysis is the possibility of treating gases under conditions preceding catalysis, i.e., under conditions such that, in the stage of treatment, there is no release of reaction products into the gas volume.

CONVERSION OF SUBSTANCES UNDER CONDITIONS OF PRECATALYSIS

The conditions of precatalysis offer a means for carrying out processes of ecological catalysis in the most energy-efficient regimes — chemisorption and prechemisorption — and also in the catalytic/desorptive regime.

In general form, a scheme for the mechanism of heterogeneous catalytic conversion reactions includes (1) a stage of adsorption of the reactants on the catalyst surface, (2) a surface reaction with the formation of reaction products on this surface, and (3) desorption of the final products into the gas phase:

\[ A + [ \ ] \rightarrow [A], \]  
\[ [A] \rightarrow [B], \]  
\[ [B] \rightarrow B + [ \ ] \]  

Here, the symbol [ ] denotes an active center of the catalyst surface. Obviously, the observed reaction rate is determined by the rate of the limiting stage, even though other, nonlimiting stages may proceed under milder conditions and at lower temperatures than those of the overall process. In such cases, the process of catalytic treatment of gases can be accomplished not only in a single-stage steady-state regime, but also through several consecutive reactions that correspond to stages of the catalytic process. For example, it has been established that the catalytic methanation of carbon monoxide over a nickel catalyst will proceed only at temperatures above 100°C, while the stage of chemisorption of reactants to form adsorbed complexes of the formaldehyde type [CH₂O] will proceed even at 75°C. These complexes, in the stage of catalysis, are reduced to methylene radicals (CH₂), which are then hydrogenated to form methane [24]. We have applied the term "adsorptive/catalytic" to catalytic gas treating processes consisting of consecutive stages that are temporally separated. The basic possibility of carrying out such processes was demonstrated experimentally in 1958 in the example of treatment of hydrogen-rich gases over a nickel catalyst to eliminate carbon monoxide [25].

Also possible in principle is the case in which the process stages (1) and (2), reflecting conversion of the target component into one of the reaction products adsorbed on the catalyst surface, proceed at a relatively low temperature. Then, as a consequence of accumulation of this product on the surface, the catalyst becomes deactivated, and it is necessary to have some means of removing the adsorbed product. In 1989 we applied the term "catalytic/desorptive" to such a process of gas treatment, consisting of consecutive stages of catalysis and desorption [26]. An example of a process that may be realized in a typical catalytic/desorptive regime is the decomposition of nitrogen oxides over transition-metal oxides. In a study of this process, using a copper—chromium catalyst, evolution of nitrogen into the gas phase was registered even at room temperature [27]. The oxygen that is formed in this reaction is completely bound to the catalyst surface, so that the reaction gradually slows down and stops. In the catalyst regeneration stage, oxygen can be removed by dissociation of the surface copper oxide and...