

On the History of Developing Catalysis in Ukraine (1850s–1980s)

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Abstract: The article is dedicated to the history of developing highly effective catalysts in the leading scientific institutions of Ukraine and explores the prerequisites for developing theories in physical chemistry, in particular those related to kinetics and catalysis. It highlights the significance of scientific discoveries at the turn of the 19th and 20th century and their application by native scientists to advance theoretical development in the field of chemistry. Special attention is paid to the works of Lev Piszarzhvskii, focusing on his advancements in electronic chemistry and, in particular, the electronic theory of catalysis. The article also outlines current challenges in creating highly efficient catalysts for the chemical and light industry, emphasizing the importance of such indicators of catalysts as activity and selectivity. Drawing on historical, scientific and patent data, the study investigates the process

of creating a highly efficient catalyst for obtaining acrylic acid from acrolein. This catalyst holds a great practical importance for the production of various polymers in industrial conditions. It is shown that, as a result of research conducted by native scientists of the Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR and the Chemistry Department of Kyiv State University, the catalyst K-2-5 was developed. The catalyst has good indicators for the industrial production of acrylic acid from acrolein. The authors also highlight works studying the properties of the obtained catalyst, specifically its porous structure, which is an important factor in catalytic processes. They extensively focus on the kinetic indicators of catalytic reactions that occur when using this catalyst. The article also emphasizes the relevance of these developments for advancing research in catalysis and chemical industrial production.

Key words: *acrolein, acrylic acid, electronic theory of catalysis, kinetics and catalysis, mechanism of catalytic reactions, porous structure of catalyst*

Introduction

Acrylic acid is the primary monomer in the production of acrylates, which are necessary for creating water-based paints, finishing preparations, as well as a number of polymers and copolymers. Polymers and copolymers derived from acrylates have a wide variety of properties: colorlessness and transparency, elasticity and strength, weather resistance and durability, making them indispensable in industries such as shipbuilding, painting, leatherwork, oil production, electronics, aviation, textiles, etc. For a long time, the widespread use of acrylic acid was limited due to the high cost of raw materials. For that reason, developing a new method for producing acrylic acid became a great concern. To solve this problem, several institutions in Ukraine investigated the process of obtaining acrylic acid through the oxidation of propylene with atmospheric oxygen.

The article is based on historical and scientific sources, using patent data. Also, our own developments in the field of physical chemistry, specifically catalysis, form a significant part of this work. The article also reviews the scientific works related to the development of industrial catalysts and their application. Particular importance is assigned to the studies carried out at the L. V. Pisarzhevskii Institute of Physical Chemistry of the Ukrainian Academy of Sciences.

Relevant research and publications

A number of works explore the history of catalysis within the context of the evolution of physical chemistry in Ukraine. Among them, several monographs should be mentioned, such as those by Barchuk *et al.* (1989), Turchenko (1957), and Orlovskiy (1959). Several publications also focus on this subject, in particular by Zabuga (2006; 2008), and Gamaliia *et al.* (2017). An article by Wisniak (2010) discusses issues surrounding the general history of catalysis. Some studies also discuss the history of kinetics and catalysis in Ukraine (Kovalenko, Chmylenko & Varhaliuk, 2011; ‘Pisarzhevskii Lev Volodymyrovych,’ 2008; Khramov, 2008). More notable publications in recent years include studies by Kovalenko, Varhaliuk and Stets (2013), and Gamaliia, Ruda and Zabuga (2023a; 2023b).

The aim of the article is to show the connection between the inventions of nineteenth- and twentieth-century Ukrainian chemists who worked in the field of catalysis, and the practical achievements in the 1980s. The mentioned publications primarily concern common issues related to the history of physical chemistry. Those related to catalysis are highlighted in these publications in the general context of this field. From our point of view, it is of interest to consider the development of catalysis in Ukraine from the middle of the 19th century to the 1980s. In addition, in our opinion, special attention should be paid to the practical advances in research at the L. V. Pisarzhevskii Institute of Physical Chemistry of Ukrainian Academy of Sciences.

On the history of catalysis: the early concepts

Catalytic processes are among the most complex ones in the field of chemistry and the chemical industry. One of the most important problems is the creation of a catalyst with predetermined properties. To accomplish this task, it is necessary to know the mechanism of the catalytic process. Initial attempts to understand the mechanisms of accelerating reactions by catalysts were made in the early 19th century (Wisniak, 2010). Even back then, a connection between adsorption and heterogeneous catalysis was discovered. The authors of the first adsorption theories of catalysis were Johann Wolfgang Döbereiner (1823) and Michael Faraday (1833).

In the mid-nineteenth century, the theory of unstable intermediates was clearly

formulated, the authors of which were Lyon Playfair (1848), as well as our compatriot Oleksiy Khodniev, professor at Kharkiv University. Khodniev tried to explain catalytic phenomena through the formation of paired intermediate compounds as a result of the reaction between the catalyst and reagents (Khodniev, 1852). This work by Khodniev is the earliest in the field of catalysis in Ukraine. He was one of the first scientists to cross the artificial boundary between ideas about chemical and physical factors determining catalytic phenomena. Viewing metabolic processes as a chain of complex catalytic processes, Khodniev diverged from the views of Berzelius, who considered catalytic phenomena a manifestation of a supernatural catalytic power, and proposed his own interpretation of catalytic processes, which included the idea of the intermediate compound formation, the idea of an active catalyst surface. Khodniev's ideas that reaction acceleration can also occur due to an increase in the concentration of reactants on the catalyst surface were progressive for that time and contributed to the development of theories related to physical catalysis.

Later, another native researcher, D. P. Turbaba (1888), confirmed that the state of equilibrium does not depend on the nature and number of catalysts, their role lies only in changing the conversion rate.

The theory of electronic chemistry

The scientific discoveries of the early 20th century gave a new impetus for the development of the catalysis theory. This was preceded by a number of theoretical and practical discoveries in the latter half of the 19th century. In this regard, an important achievement in chemical thinking in Ukraine was the formation of ideas rooted in atomism about the complex structure of the atom and its transformative ability ('Fiziko-matematicheskii fakultet...', 2008, p. 261). Development of this problem was started in the 1870s, by the eminent professor of Kharkiv University, M. M. Beketov. Speculating on the fundamental possibility of atom decomposition, Beketov only expressed doubts about the existence of sufficient energy sources for such disintegration ('Adres Ekaterinoslavskogo nauchnogo obshchestva...', 1904). The chemist O. I. Bazarov from Kyiv presented a hypothesis about the complex structure of atoms as early as in 1871. He rejected the commonly held idea of that time about chemical elements as indivisible entities. (Holub & Protsenko, 1960)

Later discoveries confirmed that these assumptions were correct. Thus, in 1895, X-rays were discovered, in 1896—radioactivity (by Henri Becquerel), and in 1898, radioactive elements and radioactive decay (by Pierre Curie, William Ramsay, Ernest Rutherford, 1902–1903). In 1903, Rutherford and Frederick Soddy identified radium as an unstable substance that decomposes with the release of other elements and energy. In 1913, Henry Moseley's law on the relationship between the properties of atoms and their spectra was established. In 1911–1913, Rutherford first experimentally studied the characteristics of the atomic structure. It was these latest discoveries that became the basis for new approaches in the field of chemistry.

The first scientists to interpret chemical processes aligning with the new ideas about the structure of atoms were Ukrainian researchers, in particular the chemist G. V. Dine, who worked as a laboratory technician at Kyiv University. As far back as in 1913, when Niels Bohr introduced his theory about atom's structure, the Ukrainian scientist approached redox reactions from the perspective of electronic representations. Dine speculated that oxidation and reduction are the result of the addition and loss of electrons.

Among the native scientists who explored this direction was Academician Lev Piszczewskii (1874–1938), an outstanding physicist and chemist, organizer, lecturer and teacher ('Piszczewskii Lev Volodymyrovych,' 2008). The development of research into the structure of matter, rejecting the ideas about the atom as an indivisible particle, became an impetus for the course of his scientific activities (Gamaliia, Ruda & Zabuga, 2023). The achievements in electronic physics and ion chemistry were applied to explain chemical phenomena and to formulate a theory of electronic chemistry (Gamaliia *et al.*, 2017).

In 1914, Piszczewskii was the first of the Ukrainian scientists to lecture on inorganic chemistry, using new electronic representations. In 1916–1917, he was a lecturer of chemistry in Katerynoslav. Based on these lectures, a textbook on inorganic chemistry for chemists was published, presenting the theory of electrolytic dissociation, taking into account the doctrine of the complex structure of the atom, and discussing redox reactions as processes of electron transfer. Piszczewskii was thus the first to introduce the electronic interpretation of redox processes and the theory of electrode potentials in practice in the educational system. In 1925, his textbook was published, presenting information from the perspective of electronic chemistry (Piszczewskii, 1925).

Pisarzhevskii's idea regarding the dependence of solid body properties on electronic structure formed the basis of the modern theory of heterogeneous catalysis. This theory had a huge impact on the formation and evolution of physical chemistry in Ukraine. The electronic theory of catalysis is based on the fact that the catalytic action of the catalyst surface is performed by the interaction of a chemisorbed organic molecule with the electrons from the solid body of the catalyst, acting as active centres for chemical interaction of molecules (Pisarzhevskii, 1956, p. 29).

Pisarzhevskii's activities in this field were mainly directed to the application of ideas from electronic chemistry to the theory of catalytic processes. Despite the enormous technological importance of catalytic reactions, the theory of catalysis was at that time in an initial stage, lagging significantly behind practical needs (Kovalenko, Varhaliuk & Stets, 2013, p. 27). In contrast to the widespread notion of heterogeneous catalysis as a purely adsorption phenomenon, Pisarzhevskii showed in a number of works that the catalytic action of solid catalysts that have electronic conductivity is a consequence of the interaction of the reacting atoms and the electrons of the catalyst crystal lattice (Kovalenko, Varhaliuk & Stets, 2013, p. 28).

Lev Pisarzhevskii's advanced ideas about the dependence of catalytic action in a solid body on its electronic structure became the basis for the further development of redox catalysis theory by scientists of his school, such as Academician V. A. Reuter and Professor M. V. Polyakov (Kovalenko, Varhaliuk & Stets, 2013, p. 29), as well as the corresponding member of the Academy of Sciences Ya. B. Gorokhovatskii and Professor V. M. Belousov.

From theoretical developments to practical application

Throughout the mid-nineteenth to late twentieth centuries, the theoretical works of Ukrainian scientists played a special role in the development of industrial catalyst for the production of acrylic acid from acrolein. It was considered economically advantageous to carry out this process in two stages: first, oxidizing propylene to acrolein, and second, oxidizing acrolein to acrylic acid. Appropriate catalysts and process conditions were selected for each stage.

Research related to solving this problem was carried out at the L. V. Pisarzhevskii Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian

SSR and by investigators of the Catalytic Oxidation Department in this Institute under the lead of Professor Belousov. It should be noted that the early twentieth-century theoretical developments in catalysis by Ukrainian chemists became foundational for the practical implementation of this task. The main methodological basis was the electronic theory by Pizarzhevskii, who was the founder and first director of the institute.

A significant part of the Ukrainian research was dedicated to developing a highly efficient competitive catalyst for the oxidation of acrolein to acrylic acid (the second stage of the process), as well as to the study of the kinetic laws of acrolein oxidation in order to use the obtained data for calculating an industrial reactor. Patent data indicates that the most promising catalysts in the oxidation of acrolein to acrylic acid are those containing vanadium and molybdenum.

First of all, data from the available literature on catalysts for the oxidation of propylene to acrolein with the following stage of obtaining acrylic acid was studied. According to the patent source on binary cobalt–molybdenum oxide catalysts, the yield of acrylic acid from the oxidation of acrolein was 40–60% (Calvin, Wood & Jenkins, 1963). With the introduction of additives, this figure increases to 80%. As shown in one of the studies (Baryshevsky & Kholyavenko, 1969), during the oxidation of propylene on complex catalysts based on cobalt molybdate, acrylic acid is obtained according to a sequential scheme at the stage of acrolein formation. In this process, the active component of the stage of oxidation of acrolein to acrylic acid on such a catalyst is cobalt molybdate.

Cobalt molybdate has several polymorphic modifications of the same composition, as described in Smith (1962) and Smith and Ibers (1965). On the basis of X-ray diffraction and IR spectroscopic data, Boutry, Daumas and Montarnal (1968) established the structures of magnesium molybdate and cobalt molybdate. Data on the methods of obtaining cobalt molybdate were also analyzed. There are three ways to obtain of this substance: (1) sintering of cobalt and molybdenum oxides; (2) precipitation from solutions of cobalt and molybdenum salts, followed by calcination of the precipitate at a temperature of about 673 K; and (3) mixing solutions of cobalt and molybdenum salts, followed by evaporation, drying and calcination.

The method of sintering oxides is inconvenient because most often a mixture of phases with an impurity of the initial oxides is obtained. The conditions of formation, some issues of kinetics, and the mechanism of developing cobalt molybdate using this method are considered in detail in Bak, Haber and

Ziolkowski (1971), Boutry, Daumas and Montarnal (1968) and Haber, Novak and Ziolkowski (1973). The properties and structure of cobalt formed during the deposition of molybdate are studied in a number of works (Corbert & Eurand, 1961; Haber, Novak & Ziolkowski, 1973; Lipsch & Schuit, 1969; Ricol, 1963; Trifirò, Caputo & Villa, 1974). By studying the behaviour of cobalt molybdate obtained by precipitation in a high-temperature X-ray chamber, new polymorphic modifications were discovered (Chojnacki & Kozłowski, 1975; Chojnacki, Kozłowski & Haber, 1974). The scheme of phase transformations of cobalt molybdate is described in Haber (1974).

The most important indicators of catalysts are activity and selectivity. The catalytic properties of the cobalt-molybdenum-oxide system have been studied in greatest detail in relation to the propylene oxidation reaction. The influence of the chemical composition of cobalt-molybdenum-oxide catalysts on their properties in the above reaction was studied by Moro-Oka *et al.* (Haber, 1974). The main products of propylene oxidation in the range of molybdenum-enriched formulations are acrolein, acrylic acid, and carbon oxides. The highest yield of acrolein was obtained on molybdenum-oxide catalyst with the ratio cobalt-molybdenum—10/90. The maximum selectivity for acrylic acid was shown by samples with the ratio cobalt-molybdenum—30/70 and 40/60. Studying these properties made it possible to determine the optimal ratios of components for an industrial catalyst (Haber, 1974).

To obtain acrylic acid from acrolein, the optimal catalyst was the one based on vanadium- molybdenum-oxide system. When analysing patent data (Kholyavenko, Belokopytov & Gerey, 1976; Tichý, Kůstka & Vencl, 1974), it was found that two compositional regions could be distinguished in the system under study that differed sharply in their catalytic properties. Samples enriched in vanadium and pure vanadium oxide were active in deep oxidation. Also, catalysts enriched in molybdenum were active in the oxidation of acrolein to acrylic acid. According to the studies, the active component of the vanadium-molybdenum-oxide system in the generation of acrylic acid was a chemical compound based on molybdenum oxide, partially substituted with vanadium.

The works dedicated to the mechanism of catalytic processes were also studied. The problem of the catalytic oxidation reaction mechanism has two main aspects: the participation of oxygen in the formation of reaction products and the conversion of the oxidized substance into products during the reaction. There are two main mechanisms for incorporating oxygen into the oxidized molecule: the stepwise alternating oxidation and reduction of the catalyst surface by the

reactants, and the confluent or associative mechanism. It has been proposed to classify the catalytic reactions mechanisms based on the presence or absence of mutual transfer of a substance between the catalyst and the reacting system, as well as the nature of this transfer.

An analysis of the data given in literature shows that most researchers support the stepwise mechanism for the formation of the selective oxidation products of hydrocarbons by alternating oxidation-reduction of the catalyst surface. Knowledge of the oxidation mechanism and the nature of the active surface of the catalyst are necessary for the scientific development of an active and selective catalyst for partial oxidation. In the heterogeneous catalytic oxidation of hydrocarbons, some general features of the mechanism inherent in various reactions and types of catalysts have been established:

1. When a hydrocarbon interacts with the catalyst surface, chemisorption occurs: weak, reversible at a given temperature, and strong, irreversible, often removed only when exposed to oxygen. The ratio of the weak and strong forms of adsorption depends on the structure of the molecule and the nature of the catalyst surface.
2. Deep oxidation of hydrocarbons is provided by weakly bound mobile oxygen, whereas mild oxidation, almost without exception, is provided by relatively strongly bound oxygen located in the lattice of oxide catalysts.
3. During the interaction of hydrocarbon and oxygen, surface compounds of different structure and with different affinity to the surface are formed on the contact surface. These compounds are active intermediate forms, caused, as a rule, by the processes of mild and deep oxidation. Moreover, the formation of the product can occur both on the surface of the catalyst and in the volume of the gas phase according to the radical chain mechanism.
4. The redox mechanism—restoration of the catalyst surface with oxidizable hydrocarbons and its re-oxidation with oxygen—is the most common mechanism of partial heterogeneous oxidation (Pisarzhevskii, 1956).
5. Works on the mechanism are closely linked to the studies on the laws governing the selection of catalysts for partial oxidation. Correlations of activity and selectivity with the binding energy of oxygen in the oxide and with the acid-base properties of the hydrocarbon and the catalyst surface are known. The most selective are the oxides of the elements of the first half of the long periods (Belousov, Kashuba & Zabuga, 1990).

The regularities listed above were used in the development of a highly efficient catalyst for the oxidation of acrolein, which was based on the well-known vanadium-molybdenum-oxide system. Generally, the process of creating such a highly efficient catalyst, excluding patent search and familiarity with the literature, can be tentatively divided into three stages: (1) search and development of the optimal chemical composition of the active mass; (2) development of an optimal method (mode) for obtaining this mass; and (3) search and selection of the optimal carrier for a given chemical composition of the active mass. These stages are intertwined, complementing each other, and their order may change.

In developing a highly efficient catalyst for the oxidation of acrolein, the possibilities of each of the three stages were almost completely used. During the preparation of catalysts, the influence of factors such as the nature and amount of the organic reductant, the amount of the active substance deposited on the support, the nature and porous structure of the support, as well as the impregnation and heat treatment regime on the activity and selectivity of the resulting contact were studied.

As a result, the catalyst named K-2-5 with yield of acrylic acid (98.7%) was developed. A particularly important property of the catalyst is the almost absolute selectivity (the absence of by-products in the reaction products), which greatly facilitates the stage of isolating the target product. The catalyst operates with consistently high performance over a wide range of water vapour (0–40%) and acrolein (1–14%) concentrations. An increase in the acrolein load makes it possible to operate the contact with high productivity, and a decrease in water vapour concentrations (down to 0%) significantly increases the concentration of acrylic acid in the reaction products, which, along with high selectivity, greatly simplifies the stage of isolating the finished product.

Investigation of the properties of catalyst K-2-5 and kinetics of the catalytic process

The creation of a highly efficient catalyst is the first step towards the implementation of scientific development in the industry. The next stage involves the calculation of an industrial reactor. This requires knowledge of kinetic laws, the study of which is given below.

The porous structure of the K-2-5 catalyst was studied using the adsorption-structural method. The most important parameters of the catalyst porosity are the specific surface area, which determines their activity, and the nature of the pore size distribution, which affects the kinetic regularities and selectivity of the catalytic process.

Almost all adsorption methods for determining the specific surface area are based on the Brunauer–Emmett–Teller (BET) theory of polymolecular adsorption. The calculation of the monolayer capacitance from the linear form of the BET equation is now generally accepted. Deviations from linearity are most often associated with the presence of micropores in the samples, in which adsorption occurs not layer by layer, but by volumetric filling of some smallest pores—micropores and supermicropores. Therefore, for such samples, the specific surface area determined by the BET method is overestimated. Nitrogen and, in particular, argon are universal in this regard; they are practically insensitive to changes in the chemistry of the catalyst surface. This is the basis of the chromatographic method for determining the specific surface by thermal desorption of nitrogen (argon).

Along with mercury pore measurement, the adsorption method of capillary condensation based on the well-known Kelvin equation was used to calculate pore volume distribution curves by size. It should be noted that the most common pore diameter found in this way and the distribution curve itself correspond only to mesoporous ones, which are filled by the mechanism of capillary condensation. The presence of microporosity in the catalysts, in which volumetric filling takes place, and macroporosity, which are not filled in the process of vapour adsorption, cannot be taken into account from the data obtained from the Kelvin equation. Therefore, the average pore size (integral value) may deviate from the calculated data in one direction or another.

For a detailed description of the adsorption-structural characteristics of the catalyst K-2-5, the methanol adsorption isotherm was obtained using a weight adsorption unit. The obtained data showed that the catalyst had pores, which was probably optimal for the oxidation of acrolein on a heterogeneous catalyst.

The study of kinetics was carried out using the flow-circulation method. The reaction products were analyzed by the chromatographic method. In terms of the previously studied catalysts, based on vanadium and molybdenum oxides, the reactions leading to the mild oxidation of hydrocarbons proceed according to the redox mechanism, while the reactions of deep oxidation proceed according to the

associative one. It can be assumed that in the case of the oxidation of acrolein to K-2-5, the reactions proceed according to the same mechanisms.

As the water concentration increases, the activity of the catalyst and the selectivity for mild oxidation products increase. The positive effect of water vapour on the processes of selective oxidation of hydrocarbons has been noticed a long time ago. However, the explanations for this fact in all the mentioned works remain hypothetical. It is likely that water, having a relatively high heat capacity, lowers the temperature of active centres and prevents deep oxidation of partial oxidation products. An increase in the concentration of water vapour in the mixture apparently promotes the desorption of reaction products from the active surface of the catalyst, thereby increasing its activity. A comparison of the data shows that the K-2-5 catalyst has a higher activity and selectivity for the formation of acrylic acid from acrolein compared to earlier catalysts. After determining the kinetic characteristics of the catalyst K-2-5, the obtained values could be used to calculate an industrial reactor.

Conclusion

As the study shows, Ukrainian scientists of the 19th–20th centuries made a significant contribution to the development of kinetics and catalysis theory. Their investigations took place within a broader context of the general development of physics and chemistry of that time and, in particular, the evolution of physical chemistry as a separate chemical branch.

Here we can trace the development path of these ideas in the field of catalysis from the very first concepts, such as the theory of intermediate compounds, to the creation of electronic theory. It is established that this theory was a consequence of fundamental discoveries in physics of the late 19th and early 20th century. Ukrainian scientists were among the first to apply the latest innovations to solve a number of issues in chemistry.

The article also highlights the role of Lev Pisarzhevskii as the founder of electronic chemistry and the first director of the Institute of Physical Chemistry. It is shown that it was Pisarzhevskii's electronic theory of catalysis that served as a theoretical basis for the creation of an industrial catalyst. Thus, a connection between the theoretical developments of previous years and solving contemporary practical problems has been firmly established. As a result of research conducted by the

institute's scientists, a highly efficient catalyst for the process of obtaining acrylic acid from acrolein was developed. Furthermore, the findings of the described studies remain relevant today owing to the demand for highly efficient catalysts for emerging technologies aimed at producing various chemical products. Specifically, further advances in the catalysis theory continue to this day.

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