

UDC 541.128.13

Outlooks and Possibilities of the Application of *in situ* Methods in Catalysis

V. V. KAICHEV

Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,
Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)

E-mail: vvk@catalysis.ru

(Received November 27, 2012)

Abstract

Methodology of *in situ* investigations aimed at the studies of heterogeneous catalytic reactions is presented. The advantage of this approach in comparison with *ex situ* studies is demonstrated with a number of examples. The outlooks and possibilities of the application of various physical methods in the *in situ* mode are considered.

Key words: heterogeneous catalysis, *in situ* methods, self-oscillations, reaction mechanisms

INTRODUCTION

The necessity to know the detailed mechanism of a reaction in order to develop efficient catalysts that would be able, under definite conditions, to provide maximal activity and selectivity in this reaction is already evident at present. Reaction mechanism means the knowledge of the nature of its active centres, key intermediates and separate stages of the catalytic process. Investigations of the detailed mechanisms of catalytic reactions became possible after the development of adsorption theory and chemical kinetics in the beginning of the 20 century. Early studies in this area were limited to kinetic measurements and determination of specific surface, chemical and phase composition of catalysts. In spite of scarce information obtained in those studies, they resulted in laying the foundations for heterogeneous catalysis. In particular, as long ago as in early 50es of the past century the concept of the chemical nature of intermediate interaction in catalysis was formulated. It says that the activity of a solid catalyst with respect to a specific reaction is determined mostly by the chemical properties of the catalyst [1].

Further development of fundamental notions on the mechanisms of heterogeneous catalytic reactions is directly connected with the application of various physical methods of investigation. The start of this stage may be assigned to the moment when the methods of vibrational spectroscopy were introduced into the practice of catalytic studies in early 1950es. Subsequent development of the experimental foundation for the development of the physicochemical parameters of catalysts and the properties of their surface opened new broad possibilities in establishing interconnections between the catalytic properties, composition and atomic structure of the particles of the active component of catalysts. We may say that it was during those years when the classical (traditional) approach to the investigations originated; it is still in use nowadays in the area of heterogeneous catalysis. This approach unites three directions of studies: the synthesis of catalysts, catalytic tests under the conditions close to real catalysis, and *ex situ* analysis of catalysts before and after reaction using a variety of physical methods.

Starting from the end of the past century, alternative approach based on investigations

carried out in the *in situ* mode is under active development in the area of catalysis. The essence of this approach is the investigation of actual working catalyst by means of various physical methods including surface-sensitive ones, under elevated (with respect to ultrahigh vacuum) pressure, directly during the catalytic process, with simultaneous analysis of the products and reagents in the gas phase. Some researchers prefer to use the term *operando* to stress that actually operating catalyst is under investigation.

ADVANTAGES AND DISADVANTAGES OF EX SITU AND IN SITU STUDIES

Undoubted advantage of *ex situ* studies is the possibility to carry out integrated investigation of catalysts using a complex of complementary methods (for example, see [2–4]). Thus, using the methods of chemical analysis and X-ray photoelectron spectroscopy (XPES) it is possible to determine the chemical composition of catalysts with high accuracy. The application of X-ray diffraction method, neutron diffraction and EXAFS [5] allows determining the phase composition and the structure of local surroundings of the atoms incorporated into the catalysts. The morphology of supports and catalysts, in particular specific surface, pore volume and size distribution, may be studied with the help of adsorption-based methods and transmission electron microscopy (TEM). A broad set of up-to-date physical methods including X-ray diffraction, energy disperse analysis, TEM, XPES, XANES [6], EXAFS, electron spectroscopy of diffuse reflection, nuclear magnetic resonance (NMR) etc. allows one to determine the shapes, sizes and chemical compositions of deposited particles, the electronic state of the active component, to study the nature of metal – support interaction, segregation effects, the reasons of unsatisfactory stability of catalysts. On the basis of the data obtained, it is possible to correct the procedures of catalyst synthesis.

At the same time, this approach has substantial disadvantages. For example, *ex situ* studies are carried out under the conditions far from the conditions of real catalysis – in vacuum or in the air at room temperature. There-

fore, it is impossible to study reaction intermediates. Moreover, catalyst state determined in the *ex situ* mode may differ substantially from catalyst state under reaction conditions.

The latter statement can be illustrated by the investigation of Ni-based catalysts for biopetroleum hydrodeoxygenation as an example [4]. The Ni 2p spectra of nickel foil and the Ni/SiO₂ catalyst are shown in Fig. 1. Curve 2 corresponds to the fresh newly synthesized catalyst. The high value of Ni 2p_{3/2} bonding energy (856 eV) and the presence of the intense lines of shake up satellites [3] in this spectrum provide evidence that in this case Ni is present mainly in Ni²⁺ state. Curve 3 corresponds to the reduced catalyst in the autoclave in the atmosphere of H₂, at 400 °C (imitation of reaction medium) followed by passivation with ethanol. It should be noted that this catalyst was in contact with air during transfer from autoclave to the spectrometer. Therefore, the spectrum of Ni 2p contains only a small peak in the region of 853 eV, corresponding to Ni in the metal state. The major part of nickel in the subsur-

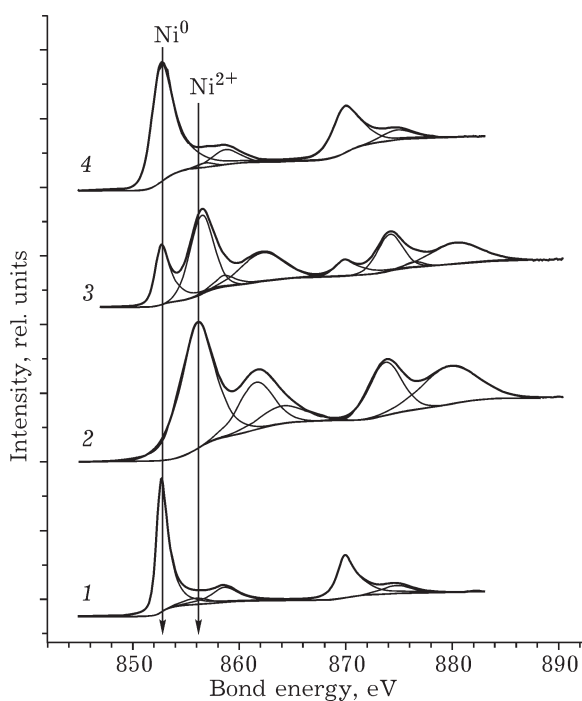


Fig. 1. Ni 2p spectra of nickel foil (1) and Ni/SiO₂ catalyst (2–4): 2 – fresh catalyst; 3 – reduced in the autoclave in H₂ (1 atm) at 400 °C, followed by contact with the air; 4 – reduced in the high-pressure cell of XPES spectrometer under the same conditions.

face region is present in the oxidized state (~73 %). Curve 4 corresponds to the spectrum obtained after the reduction of the catalyst in the high-pressure cell of the XPES instrument under the same conditions [4]. However, after evacuation of H₂ the catalyst was transferred into the analytical chamber of the spectrometer without any contact with the air. One can see that in this case Ni is present in the subsurface layer of the catalyst mainly in the metal state. It follows from these data that the state of the active component of the catalyst can be substantially dependent on the conditions of its examination.

In order to eliminate the disadvantages listed above, it is necessary to carry out examination in the *in situ* mode. This approach has several advantages:

1. The use of surface-sensitive methods in the *in situ* mode allows one to determine the nature and concentration of reactive intermediates adsorbed on catalyst surface, and to study chemical processes that take place on the surface of the working catalyst.

2. The major routes and rates of catalytic reactions may be determined by analysing the products and reagents in the gas phase.

3. The investigation of catalyst state in the *in situ* mode allows unambiguous determination of the nature of active centres by plotting the correlation between chemical composition, structure and morphology of the catalyst, and its catalytic action.

It should be noted that this approach is under active introduction into the practice of research during the past 15 years. However, as the transition to *in situ* studies requires the development of specialized equipment, which is rather complicated and expensive as a rule, the results of *in situ* studies still remain unique.

OUTLOOKS AND POSSIBILITIES OF VARIOUS PHYSICAL METHODS IN THE *IN SITU* MODE

From the viewpoint of arrangement of the *in situ* experiments, the physical methods of the investigation of solids may be divided into several groups:

- 1) microscopic methods (TEM, scanning electron microscopy, scanning probe microscopy *etc.*);

- 2) magnetic methods (NMR, magnetic susceptibility measurements *etc.*);

- 3) X-ray methods based on rigid X-ray radiation with the quantum energy above 5000 eV (X-ray diffraction methods, EXAFS, XANES, neutron diffraction *etc.*);

- 4) optical spectral methods (IR spectroscopy, sum frequency generation spectroscopy, Raman spectroscopy, electron spectroscopy in the UV and visible ranges including diffuse reflectance electron spectroscopy *etc.*);

- 5) surface-active methods based on detection of electrons with the energy below 1500 eV (XPES, XANES *etc.*).

Almost each method has its own shortcomings and difficulties with respect to its implementation in the *in situ* mode. For example, all the microscopic methods are not used in the *in situ* mode for different reasons. Optical spectroscopy cannot be used due to insufficient spatial resolution. Optical microscope in the visible light allows one to distinguish the structures with the minimal distance between elements about 0.2 μm. Due to the use of electron beam with the energy 1 to 100 keV instead of the light beam, scanning electron microscope possesses substantially larger magnification than the optical microscope. At present the best models provide the spatial resolution at a level of 1 nm [7]. However, it is evident that this is insufficient too for the investigation of the mechanism of catalytic reactions. Moreover, the limiting resolution is achieved only when flat conducting samples are studied. As a result, scanning electron microscopy is most often used in catalysis to study the structure of catalyst granules or the processes involved in catalytic corrosion.

Transmission electron microscope provides high spatial resolution, which allows distinguishing separate atoms and molecules. Modern models ensure the spatial resolution less than 1 Å. The principle of its operation is based on the formation of the image as a result of passing the high-energy electron beam (100 keV to 1 MeV) through a thin sample. Due to electron scattering on the atoms and molecules in the gas phase, transmission electron microscopy in the standard arrangement is able to operate only under ultrahigh vacuum (UHV). However, recently the models of microscopes appeared that are equipped with corresponding cells and systems of differential evacuation, which allow obtaining spatial resolution at a lev-

el of 1.5 Å at a pressure of 1 to 50 Pa [8]. In particular, the reconstruction of gold surface under the conditions of CO oxidation was demonstrated. At the same time, there are no reports in the literature that would describe the analysis of catalytic properties simultaneously with the examination of the morphology of catalysts by means of TEM at increased pressures. Taking into account the rapid development of technology, one may expect the first *in situ* studies of the mechanisms of heterogeneous catalytic reactions using TEM to appear in the nearest future.

The methods of scanning probe microscopy possess a definite potential for use in the *in situ* mode [9]. Scanning probe microscopes form a class of microscopes for obtaining the image of the surface and its local characteristics. The process of image formation is based on surface scanning by the probe. In the general case, the method allows one to obtain a three-dimensional image of the surface (topography) with high resolution. The most widespread methods are those of scanning tunnelling microscopy (STM) and atomic force microscopy. In STM, a sharp metal needle is driven close to the sample at a distance of several angstroms. When small (with respect to the sample) potential is supplied to the needle, tunnelling current arises. The current strength is exponentially dependent on the distance. Typical values of current strength are 1 to 100 pA at a distance of about 1 Å. During scanning, the needle moves over the sample surface. In this case, it is possible, for example, to measure the strength of tunnelling current and then to calculate the distance to the sample.

It is important to stress that STM indeed provides obtaining the image of surface with the atomic resolution within a broad range of pressure values. The difficulties connected with the use of scanning tunnelling microscopy for *in situ* studies are first of all due to technical hindrance in coupling the microscopes with other methods. This is connected with the fact that the scanners of microscopes are very sensitive to vibrations and thermal drift. Therefore, after heating the sample to a definite temperature, some time is necessary (several hours) for thermal drift to attenuate. As a result, the use of SRM *in situ* does not allow achieving atomic resolution for metals, which hinders the anal-

ysis of data obtained. For example, studying the oxidation of CO on Pt(110) in the *in situ* mode by means of STM [9] it was concluded that the surface platinum oxide is formed. However, later on, it was demonstrated using *in situ* XPES that platinum remains in the metal state under reaction conditions [10].

In this connection, at present STM studies are carried out at room temperature or even at cryogenic temperatures, though modern models may operate within the range 50 to 1000 K. In addition, probe microscopy methods are applicable only to study flat model catalysts. Nevertheless, STM is extensively used to characterize flat model catalysts that are used further on to carry out model *in situ* studies. Metal clusters deposited onto highly oriented pyrolytic graphite or onto thin oxide films formed on the surface of the single crystals of metals and alloys are most frequently involved [7, 11]. By present, the procedures allowing one to spray metal particles of required size with narrow size distribution have been already developed. The narrow size distribution is extremely important for the studies of the dimension effect in catalysis.

Among magnetic methods, NMR is most actively used to carry out *in situ* studies [12, 13]. Nuclear magnetic resonance is the resonant absorption or emission of electromagnetic energy by a substance containing nuclei with non-zero spin, in the external magnetic field. For example, the nuclei possessing non-zero nuclear magnetic moment are ^1H , ^3H , ^{13}C , ^{14}N , ^{15}N , ^{19}F , ^{29}Si , ^{31}P etc. In the simplest case of a NMR experiment, a sample in an ampoule is placed in the constant uniform magnetic field overlapped by a weak radio frequency field. The bands of resonant absorption are determined by varying the frequency of radio frequency field.

High-resolution *in situ* NMR spectroscopy in solids is actively used to study the kinetics and mechanisms of hydrocarbon transformations on the surface of solid catalysts [12, 13]. It should be noted that this is expensive and very complicated technique requiring the presence of highly skilled researchers. As a rule, NMR on ^{13}C and ^1H nuclei is studied. To improve the resolution, it is necessary to use the additional procedure of sample rotation under the magic angle during the studies. High resolution NMR spectra usually consist of narrow and well-re-

solved lines corresponding to magnetic nuclei in different chemical surroundings. The intensities (areas) of signals in the spectra are proportional to the number of magnetic nuclei in each grouping. Correspondingly, the method allows identification of hydrocarbons in the adsorbed state, that is, reaction intermediates, and the kinetics of their transformations. The major disadvantage of this method is that it is very difficult to combine NMR in the *in situ* mode with any other method. The ampoule with the sample rotates with the frequency of 2–20 kHz, which hinders the use of flow regime. Pressure in sealed ampoules at a temperature of 300 °C may reach 20 atm [13]. One of the examples may be the work describing *in situ* investigation of the mechanism of isotope exchange demonstrating that hydrogen atoms of methyl groups and one methylene group of adsorbed propane participate in exchange directly with Brønsted acidic centres of zeolite independently of each other [13].

Among structural methods, it is necessary to mention X-ray diffraction which is increasingly frequently used in the *in situ* mode [14]. It is based on the diffraction of X-rays on the lattice of a solid. The standard instrument is composed of the X-ray tube, goniometer and the detector of X-ray radiation. Powder X-ray diffraction is most frequently used in catalysis. This method studies the structural characteristics of

a material with the help of X-ray diffraction on a powdered or polycrystalline sample of the material under study. The dependence of the intensity of scattered radiation on scattering angle is revealed as a result of experiment. Using well known Wulf-Bragg and Sherrer formulas, one may easily recalculate the positions of peaks and their width into interplanar spacings and corresponding coherent lengths, and thus it is possible to obtain the information on the phase composition and sizes of particles.

Powder X-ray diffraction is widely used to determine the phase composition of catalysts in the *in situ* mode. At the same time, the majority of modern diffractometers can be easily adapted to *in situ* studies. For this purpose, it is sufficient to equip the instruments with the following units:

1) a special cell (reaction chamber) inside which there is the sample under study; it allows measurements in the flow of the reaction mixture of required composition within a broad range of pressure and temperature values;

2) the system of gas preparation and admission into the cell, including pressure vessels, reducers, gas pipelines, pressure sensor, gas flow regulators, forepump (desirably providing oil-free pumping) *etc.*;

3) gas composition analysers based on mass spectrometer or gas chromatograph.

The most complicated part of the work aimed at the introduction of *in situ* techniques

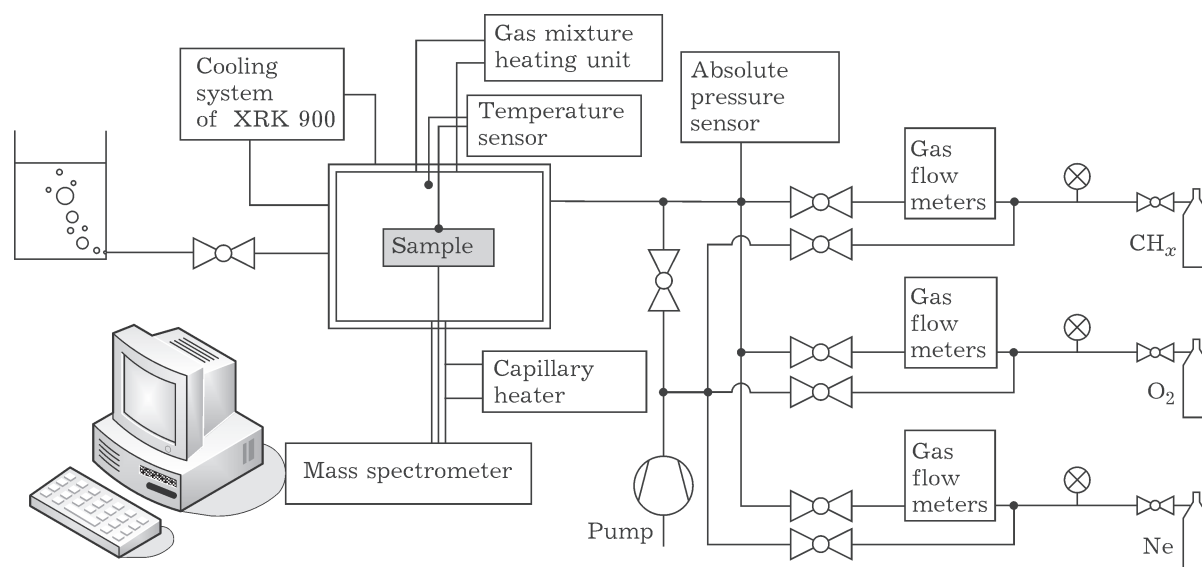


Fig. 2. Scheme of the set-up based on reaction chamber XRK-900 for *in situ* studies of the mechanisms of heterogeneous catalytic reactions by means of X-ray diffraction.

is the development and construction of the cell allowing measurements in this mode. Other parts of the set-up are assembled from standard units. If any experience in designing is absent, it is possible to use commercially available cell, for example Anton Paar XRK-900 which allows one to carry out measurements at the pressure of reaction mixture up to 10 atm within temperature range 0 to 900 °C. The scheme of the simplest system for *in situ* X-ray diffraction measurements based on XRK-900 reaction chamber and SRS UGA-100 mass spectrometer is shown in Fig. 2. This system was mounted at the Station of high-precision X-ray diffractometry of the Siberian Centre for Synchrotron and Terahertz Radiation (channel No. 6 of VEPP-3 storage, INP of the SB RAS, Novosibirsk). Similar equipment may be used also to adapt XANES and EXAFS spectrometers to *in situ* studies.

It should be noted that the studies of various phase transitions and chemical transformations in solids under the action of temperature and reaction mixture are often presented as *in situ* [4]. However, in catalysis the term *in situ* is understood as simultaneous investigation of the structure, chemical composition and catalytic properties. From this point of view, analysis of the gas phase during *in situ* studies is a compulsory condition. As example, we may consider *in situ* investigation of NdCu₂ catalyst in the reaction of CO hydrogenation [14]. Using X-ray phase analysis in combination with gas chromatography, the authors demonstrated that catalyst activation leading to an increase in CH₃OH yield is determined by the formation of metal copper phase on Nd₂O₃ surface. The studies were carried out at a pressure of 15 bar at 423 K.

Optical spectral methods are most actively used in the *in situ* studies because of relative simplicity of arrangement [15–19]. Their major disadvantage is the absence of sensitivity to elements, which often causes ambiguous data interpretation. In addition, it is difficult to achieve a good signal to noise ratio when working in the region of high pressure (1 atm and above) due to the absorption of radiation in the gas phase. Nevertheless, these methods are actively used to analyze adsorbed molecules and particles on catalyst surface in the *in situ* mode. Two methods of vibrational spectroscopy that are actively developing abroad are worth men-

tioning: Sum Frequency Generation (SFG) and Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRAS) [18]. In Russian these methods are called GSF spectroscopy (sum frequency spectroscopy [19]) and reflectance IR spectroscopy in the version of polarization modulation, respectively.

The former method is based on the second-order nonlinear process. For this process to manifest itself, it is necessary that two laser pulses get simultaneously at the same point at the surface. Absorbing two quanta of the IR and visible radiation, the system undergoes transition to some virtual level. The reverse transition of the system is accompanied by the emission of a quantum with the energy corresponding to the sum frequency. The frequency of laser radiation in the visible region remains constant during recording, while the frequency of IR laser varies within a definite range. The intensity of the SFG signal is quadratically dependent on the coefficient of nonlinear susceptibility and is proportional to the intensity of both visible and infrared radiation. According to selection rules, the vibrations that are active either in IR or in Raman spectroscopy manifest themselves in SFG spectra. It is important to stress that SFG signal does not arise if there is inversion symmetry in the system. Because the majority of metals have face-centred cubic lattice with central symmetry, SFG spectrum depicts only the vibrational states of adsorbed molecules. The gas phase does not contribute into SFG spectrum, too. Therefore, it is possible to obtain the vibrational spectra of adsorbates *in situ* at a pressure up to 1 atm and even higher [18, 19].

The latter method, PM-IRAS, also allows one to carry out *in situ* studies at increased pressure. It is known that the absorption of electromagnetic radiation occurs through the excitation of vibrations if the derivative of the dipole moment over normal coordinates is different from zero. In the studies of adsorbed molecules on the metal surface, an additional selection rule arises as a consequence of screening the dipole oriented parallel to the surface: the perpendicular component of the derivative of dipole moment over normal coordinates must be different from zero. Correspondingly, the maximal signal of the absorption of IR radia-

tion is observed in the case of sliding *p*-polarized radiation. This principle lays the ground for PM-IRAS method: absorption spectra are recorded in the mode of polarization modulation. The signal recorded during *s*-polarized light incidence contains the information mainly about absorption in the gas phase, while the signal recorded with *p*-polarized light contains the information about both the gas phase and adsorbed particles. Therefore, the difference signal (*p*-*s*) contains only the absorption signal of adsorbates. So, PM-IRAS method allows detecting intermediates adsorbed on the surface, as well as the products and reagents in the gas phase. Due to this fact, conversion and selectivity of catalytic processes may be calculated [18].

Both methods are successfully used in the *in situ* studies of the mechanisms of heterogeneous catalytic reactions. For example, the authors of [18, 19] describe the results of the studies of methanol decomposition and oxidation on palladium surface using these methods. It is shown that methanol decomposition follows two competing routes: rapid dehydrogenation to form CO and decomposition with C-O bond rupture. In the latter case methyl groups are formed; even at room temperature they are dehydrogenated to form carbon. In the presence of oxygen, partial oxidation of CO and hydrogen (the products of complete dehydrogenation) to CO₂ and water occurs, and also desorption of formaldehyde (the product of partial dehydrogenation) into the gas phase.

In the *in situ* studies, the methods of vibrational spectroscopy are well supplemented by XFES [18, 19]. This method is element-sensitive; it is actively used to determine the chemical composition of solids [20]. It is based on the external photoeffect phenomenon. Irradiation of the surface with monochromatic X-ray radiation occurs during experiment, which causes electron emission. On the basis of the data on the energy of incident and emitted photoelectrons, it is possible to calculate the energy of electron bonding in the substance under study. Each element except hydrogen and helium has a definite set of lines; their exact positions are determined by the local chemical surroundings, while the intensity is proportional to the number of atoms in the zone under analysis. Because of this, it is possible to determine the

chemical composition of solids with the help of XPES. The depth of analysis is determined by the free path of photoelectrons in the solid and equals 2 to 5 nm. Therefore, this method is surface-sensitive and allows studying not only the chemical composition of subsurface catalyst layers but also adsorbates on its surface.

Due to photoelectron scattering on gas molecules, standard XPES spectrometers can be used only to record spectra in vacuum. The free

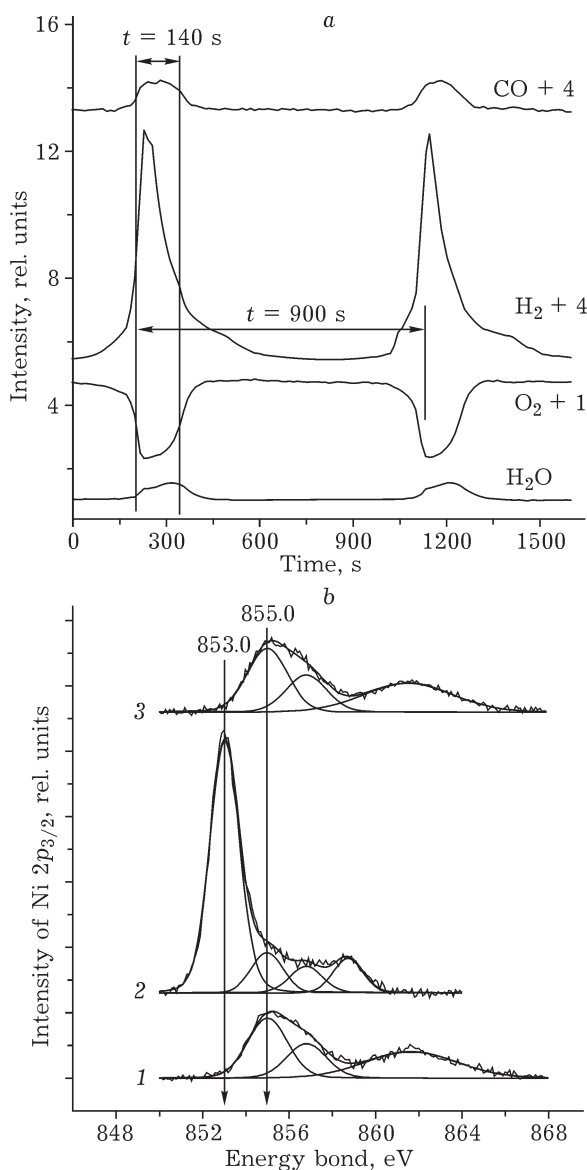


Fig. 3. Typical appearance of the oscillations of the concentrations of oxygen and the products of propane oxidation (CO, H₂, H₂O) on nickel foil (a) and Ni 2p spectra (b) recorded during different time intervals. Time, s: 700–900 (1), 1150–1200 (2) and 1400–1500 (3); $T = 620^\circ\text{C}$, $\text{CH}_3\text{H}_8/\text{O}_2 = 3 : 1$, $P = 0.5$ mbar.

path of electrons in gas depends on their kinetic energy, pressure, temperature, and the cross section of scattering of gas molecules. For example, at a pressure of 10 mbar the free path is several tenths of a millimetre. Therefore, for *in situ* studies it is necessary to use the spectrometers of special design in which the path of photoelectrons in the range of higher pressures is sufficiently short [21–24]. To achieve this goal, special cells and systems of differential pumping are used. The use of the synchrotron radiation of high brightness allows one to increase the pressure of reaction mixture above the sample during recording the spectra to 100 mbar [23].

One of the examples of the use of XPES may be the *in situ* investigation of propane oxidation on Ni [25]. It was demonstrated previously that under definite conditions this reaction proceeds in the mode of auto-oscillations; however, the reasons of auto-oscillation remained unclear [26]. It was demonstrated with the help of XPES in the *ex situ* mode that the surface of the catalyst (Ni foil) is coated with oxide layer both before and after reaction. However, it was demonstrated unambiguously during *in situ* studies that nickel is present in the metal state during the active semi-periods corresponding to the high rate of propane oxidation; the transition into the inactive state was accompanied by the formation of NiO layer not less than 3 nm thick on catalyst surface. Typical oscillations of the pressure of reagents and products are shown in Fig. 3, along with Ni 2p spectra obtained during the semi-periods of high and low activity of propane oxidation. One can see that the origin of auto-oscillations is caused by the periodic reversible oxidation of Ni to form NiO.

CONCLUSION

It is demonstrated that a series of physical methods, such as X-ray structural analysis, EXAFS, XPES, SFG, PM IRAS *etc.* in combination with mass spectrometry and/or gas chromatography can be successfully used to study the mechanisms of heterogeneous catalytic reactions at increased (in comparison with ultra-high vacuum) pressures in the *in situ* mode. Within one experiment, it is possible to

determine the state of the catalyst, the nature of active component, key intermediates and major reaction routes. Typical examples of *in situ* studies are described in [17–25] where, in particular, CO hydrogenation, ethane hydrogenation and methane oxidation are considered, as well as methanol decomposition and oxidation on Pd, selective oxidation of methanol into formaldehyde on Cu, CO and methanol oxidation on Ru, ethylene epoxidation on Ag and propane oxidation on Ni. Those results point to the promising character of the development of *in situ* methods in heterogeneous catalysis.

REFERENCES

- 1 Boreskov G. K., Kataliz. Voprosy Teorii i Praktiki. Izbrannye Trudy, Nauka, Novosibirsk, 1987.
- 2 Borchert H., Frolova Yu. V., Kaichev V. V., Prosvirin I. P., Alikina G. M., Lukashevich A. I., Zaikovskii V. I., Moroz E. M., Trukhan S. N., Ivanov V. P., Paukshtis E. A., Bukhtiyarov V. I., Sadykov V. A., *J. Phys. Chem. B*, 109 (2005) 5728.
- 3 Khassin A. A., Yurieva T. M., Kaichev V. V., Zaikovskii V. I., Demeshkina M. P., Minyukova T. P., Baronskaya N. A., Bukhtiyarov V. I., Parmon V. N., *Kinetika i Kataliz*, 47, 3 (2006) 420.
- 4 Bykova M. V., Ermakov D. Yu., Kaichev V. V., Bulavchenko O. A., Saraev A. A., Lebedev M. Yu., Yakovlev V. A., *Appl. Catal. B*, 113?114 (2012) 296.
- 5 EXAFS – Extended X-ray Absorption Fine Structure – Strukturny Metod, Osnovanny na Analize Dalney Tonkoy Struktury Rentgenovskikh Spektrov Pogloshcheniya.
- 6 XANES – X-ray Absorption Near-Edge Structure – Metod Issledovaniya Elektronnogo Stroyeniya Atomov, Molekul i Tverdykh Tel, Osnovanny na Analize Blizhney Tonkoy Struktury Rentgenovskikh Spektrov Pogloshcheniya.
- 7 Demidov D. V., Prosvirin I. P., Sorokin A. M., Bukhtiyarov V. I., *Catal. Sci. Technol.*, 1 (2011) 1432.
- 8 Fujita T., Guan P., McKenna K., Lang X., Hirata A., Zhang L., Tokunaga T., Arai S., Yamamoto Y., Tanaka N., Ishikawa Y., Asao N., Yamamoto Y., Erlebacher J., Chen M., *Nature Mater.*, 11 (2012) 775.
- 9 Hendriksen B. L. M., Bobaru S. C., Frenken J. W. M., *Catal. Today*, 105 (2005) 234.
- 10 Chung J.-Y., Aksoy F., Grass M. E., Kondoh H., Ross P., Jr., Liu Z., Mun B. S., *Surf. Sci.*, 603 (2009) L35.
- 11 Baumer M., Freund H.-J., *Progress Surf. Sci.*, 61 (1999) 127.
- 12 Hunger M., Weitkamp J., *Ang. Chem. Int. Ed.*, 40 (2001) 2954.
- 13 Stepanov A. G., Parmon V. N., Froyde D., *Kinetika i Kataliz*, 48 (2007) 554.
- 14 Nix R. M., Rayment T., Lambert R. M., Jennings J. R., Owen G., *J. Catal.*, 106 (1987) 216.
- 15 Melsheimer J., Mahmoud S. S., Mestl G., Schlügl R., *Catal. Lett.*, 60 (1999) 103.
- 16 Hunger M., Weitkamp J., *Angew. Chem. Int. Ed.*, 40 (2001) 2954.

- 17 Tinnemans S. J., Mesu J. G., Kirvinen K., Visser T., Nijhuis T. A., Beale A. M., Keller D. E., van der Eerden A. M. J., Weckhuysen B. M., *Catal. Today*, 113 (2006) 3.
- 18 Rupprechter G., *Adv. Catal.*, 51 (2007) 133.
- 19 Kaichev V. V., Bukhtiyarov V. I., Rupprechter G., Freund H.-J., *Kinetika i Kataliz*, 46 (2005) 288.
- 20 Minachev Kh. M., Antoshin G. V., Shpiro E. S., *Fotoelektronnaya Spektroskopiya i Yeye Primeneniye v Katalize*, Nauka, Moscow, 1981.
- 21 Knop-Gericke A., Kleimenov E., Hävecker M., Blume R., Teschner D., Zafeiratos S., Schlögl R., Bukhtiyarov V. I., Kaichev V. V., Prosvirin I. P., Nizovskii A. I., Bluhm H., Barinov A., Dudin P., Kiskinova M., *Adv. Catal.*, 52 (2009) 213.
- 22 Kaichev V. V., Prosvirin I. P., Bukhtiyarov V. I., *Zh. Struk. Khim.*, 52, Suppl. (2011) S94.
- 23 Bluhm H., Hävecker M., Knop-Gericke A., Kiskinova M., Schlögl R., Salmeron M., *MRS Bull.*, 32 (2007) 1022.
- 24 Bluhm H., Hävecker M., Knop-Gericke A., Kleimenov E., Schlögl R., Teschner D., Bukhtiyarov V. I., Ogletree D. F., Salmeron M., *J. Phys. Chem. B.*, 108 (2004) 14340.
- 25 Kaichev V. V., Gladky A. Yu., Prosvirin I. P., Saraev A. A., Hävecker M., Knop-Gericke A., Schlögl R., Bukhtiyarov V. I., *Surf. Sci.*, 609 (2013) 113.
- 26 Gladky A. Yu., Kaichev V. V., Ermolaev V. K., Bukhtiyarov V. I., Parmon V. N., *Kinetika i Kataliz*, 46 (2005) 269.