

*Teaching Experiment in Science
Учебен експеримент в природните науки*

TUNING THE ELECTRONIC PROPERTIES OF HETEROGENEOUS CATALYSTS: AN AUTHENTIC RESEARCH-BASED LABORATORY COURSE

Paweł Bernard, Gabriela Grzybek, Paweł Stelmachowski
Jagiellonian University, Poland

Abstract. The surface properties of a material play a key role in heterogeneous catalysis. The presented experiment demonstrates tuning of the electronic properties of the catalyst by surface doping with alkali. In spite of the addition of minimal amounts of the selected promoter, its influence on the activity of the catalyst is enormous. The experiment offers not only a good opportunity to familiarize students with the procedure of catalytic tests and the work function measurements of the material, but also is the base for open ended Authentic Research-Based students' investigations. The experiment was introduced to students of the 3rd year of chemistry who specialize in Inorganic and Structural Chemistry. It is one of the experiments performed during so-called Open Laboratory classes, which aim is to prepare students for independent bachelor research. The scientific content and method of implementation of the experiment was evaluated. An evaluation was based on questionnaire survey containing Plus, Minus, Interesting tool (PMI) and assessment of difficulty and load of work that is necessary to complete the experiment. The survey was followed by short interview about skills and knowledge gained during the experiment.

Keywords: undergraduate chemistry, research-based laboratory, heterogeneous catalysis, surface science, materials science

Introduction

The presented experiment aims at demonstrating a method of tuning the catalytic properties of a substance in the gas-solid catalysed reaction by the addition of minimal amount of the selected promoter. The heterogeneous catalysis is an important area of chemical processes, because of both the essence of the investigated reactions and its industrial applications. Due to its complexity, the heterogeneous catalysis is not often the subject of student laboratory practice, but there are examples of successful experiments used in education (Laursen, 2011; Moura, 2006; Mattson, 2006; Fischer, 2003; Raymundo-Pinero, 1999; Okumura, 1996). The experiment described in this paper offers a good opportunity to familiarize students with the procedure of both catalytic tests, and the work function measurements of the material and the possibility of cor-

relation of those two parameters in the case of redox reactions. As a main process, the decomposition of nitrogen(I) oxide into its constituent elements over solid catalysts was chosen. The reaction is an important part of many industrial processes, including synthesis and exhaust gas control (Pérez-Ramírez et al., 2003; Parmon et al., 2005). The described below variant of the experiment shows the relation between number of nominal potassium atoms per surface area unit of Co_3O_4 spinel and its catalytic activity. The relation is well described in the literature (Stelmachowski et al., 2009), and the experiment can be easily modified and influence other parameters on catalytic activity can be investigated, ex: type of alkali metal, type of spinel, type of doping agent (electropositive vs. electronegative) etc.

The described experiment was introduced for the first time to students at Jagiellonian University in 2010. It is one of investigations that are in the basic programme of the so-called Open Laboratory. This subject is obligatory for students at the last year of bachelor studies in Chemistry with a specialisation in the Inorganic and Structural Chemistry. The aim of the Open Laboratory is to simulate the organization of work during research for a bachelor thesis, acquaint students with the specification and usage of research equipment available at the department, the methodology of scientific research and the publication of results. All experiments in the course have character of Authentic Research-Based Laboratory (Brownell et al., 2012), and are focused on the independent research of students. At the first meeting, students receive a framework of experimental area in which they have to complete investigations during semester. Students are divided into groups, maximum 4 persons per group. The organization of the research is left to the students. In the described experiment they have to share responsibilities and schedule work including literature review, plan of the investigations, conduct the research, make analyses and write the report. Students can use a guide including procedure for the synthesis of doped cobalt spinel, work function measurements, catalytic tests and report requirements. Research apparatus with support of technicians and tutors are available to them in given time periods – at least one period per week in the course of the experiment plus some additional time depending on the hardware availability. Their work is supervised by tutors; students can get support from the tutors at any stage of their work. The assessment is based on the final report and tutors' observations. The report is in the form of internal scientific publication.

The experiment

Basic information

N_2O being considered the third most important greenhouse gas and destroyer of the ozone layer is emitted, among other sources, from nitric acid plants, where it is formed as a by-product during ammonia oxidation. Catalysts for low temperature decomposition

of nitrogen(I) oxide are constantly being developed and the most promising are those based on cobalt spinel, Co_3O_4 . The mechanism of nitrogen(I) oxide decomposition over oxides containing transition metal ions (TMI) can proceed via electron transfer route, which in its simplest form consists of three steps: dissociation of the N_2O molecule (Eq. (1)), the diffusion of surface oxygen intermediates and their recombination with the subsequent desorption of molecular oxygen (Eq. (2)).



Initiation of the reaction occurs at the redox centres with the electron transfer from the catalyst to the anti-bonding orbital of the N_2O molecule, which leads to the cleavage of the NN–O bond and release of the nitrogen molecule. The catalytic cycle can be closed by the diffusion and recombination of surface oxygen intermediates (the Langmuir–Hinshelwood mechanism) followed by desorption of molecular oxygen (Pietrzyk et al., 2007; Piskorz et al., 2008). All these steps can be regarded as a redox process (electron transfer from and towards the surface), thus they depend strongly on the electronic properties of the catalyst surface (Stelmachowski, 2009).

The electronic properties of metallic and non-metallic surfaces can be modified by the deposition of alkali promoters (AMs) which alter the work function of the solid. The work function is defined as the minimum energy required moving an electron from the Fermi level into vacuum. Its value gives information about the electronic properties of the solid surface. The promotional effect of alkali is mainly related to their low ionization potentials which allows for a charge transfer to the catalyst surface, inducing an electric field gradient at the surface, generated by the resulting dipole moment. This is especially pronounced in the case of heavier alkali atoms due to their large ionic radii which in turn gives rise to large values of the dipole moment and the associated work function changes (Somorjai 1994; Zasada et al., 2009; Kotarba et al., 2004).

For the simplicity of the picture, the adsorption of alkali metals on metal surfaces (instead of that of the oxides), will be elaborated below. The simplest model, developed by Langmuir and Gurney in the 1930s predicts a partial transfer of charge from the AM to the substrate at very low coverage, and the subsequent depolarization of these atoms due to their mutual interactions as the coverage is increased. Although this model is a simplified one it can be used to demonstrate a formation of a surface dipole, where an alkali atom (or molecules, such as NO or NO_2) loses part of its valence electron density and a dipole moment associated with the positively polarized adsorbate atom is formed (Huang et al., 2008). On the other hand, halogens are the chemical elements that have

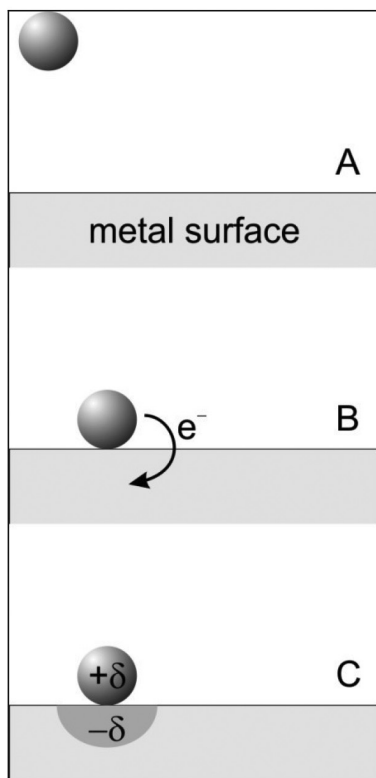


Fig. 1. Schematic illustration of localized surface dipole formation due to adsorption of alkali atom on metallic surface. A) AM and surface separated; B) Electron density transfer from AM to the surface; C) Formation of a localized surface dipole

the strongest tendency to ionize by taking in an electron. Therefore, it is rather likely that a halogen atom (or molecules such as O_2) adsorbed on a metal surface acquires a negative charge that creates a local dipole with a dipole moment pointing into the bulk, which then increases the work function of the metal surface (Roman & Groß, 2013). In the case of metal oxides the picture complicates, but principles are remained the same (Breedon et al., 2009; Bredow et al., 1998; Sensato et al., 2002). When adsorbates induce a positive work function change upon adsorption, they are expected to withdraw electrons from the surface. Conversely, a negative work function change arises from a donation of charge from the adsorbate to the surface. The more recent picture describes work function modifications due to significant depopulation (population) of states along the band gap. In this process, the chemisorbed species are shown to trap holes (electrons) producing an electron-accumulated (electron-depleted) space-charge layer in the outer surface region of the material. Such a charge separation is responsible for the decrease (formation) of a potential barrier at the interface (Breedon, 2009; Bredow, 1998; Sensato,

2002). In the Fig. 1 the schematic formation of localized surface dipole is presented for a model case of alkali metal and metallic surface. When the alkali is deposited from a chemical compound (hydroxide, carbonate, etc.) the corresponding anion remains in vicinity on the surface to compensate for the electric charge.

In this experiment, it is demonstrated how the reactivity of cobalt spinel can be tuned by controlled doping with potassium carbonate. The catalytic activity in the N_2O decomposition is correlated with the changes of the chemical potential of the electrons at the Fermi level (work function) of the K-doped Co_3O_4 .

Synthesis

Commercial Co_3O_4 can be used. Alternatively, spinel Co_3O_4 can be synthesized by the thermal decomposition of cobalt carbonate by heating in air at 773 K for 5 hours (El-Shobaky & Turkey, 2002). In both cases, product specific surface area tests are required.

The potassium doped cobalt spinel samples should be obtained in the range of $n_K = 0 - 10$ atoms/nm². This can be achieved by incipient wetness impregnation from K_2CO_3 by introducing 1 cm³ of its solution with various concentrations (c) [mol·dm⁻³], calculated from equation 3, into 1 g of the spinel catalyst. The potassium-doped cobalt spinel samples will be labelled as n_K -K/ Co_3O_4 .

$$c = \frac{n_K \cdot S_{BET} \cdot m_{Co_3O_4} \cdot 10^{21}}{2 \cdot V_l \cdot N_A} \quad (3)$$

where: n_K (nm⁻²) – number of potassium atoms per nm²; S (m²·g⁻¹) – specific surface area; $m_{Co_3O_4}$ (g) – mass of cobalt spinel; V_l (cm³) – potassium carbonate solution volume; N_A (mol⁻¹) – Avogadro constant = $6.02 \cdot 10^{23}$.

The figure ‘2’ in the denominator of Eq. (3) comes from the stoichiometry of the potassium carbonate where one molecule of K_2CO_3 contains two atoms of potassium. Moreover, the coefficient 10^{21} originates from bringing to the common units. The promoted samples need to be dried at 373 K for 0.5 h and next calcinated at 673 K for 4 h.

Reactivity

Reactivity tests are performed in an apparatus dedicated for temperature programmed experiments with on-line gas phase composition detection. This kind of setup is described by Young (2009), and the only modifications are: (i) the source gases: a prepared mixture of N_2O (5% in He or Ar) or non-diluted N_2O and He with subsequent mixing of the two gases; (ii) a catalytic reactor. The quartz reactor of a design similar to that shown in Fig. 2 can perform as a steady state reactor with ideal mixing (Davis & Davis, 2003) which facilitates the interpretation of the obtained data.

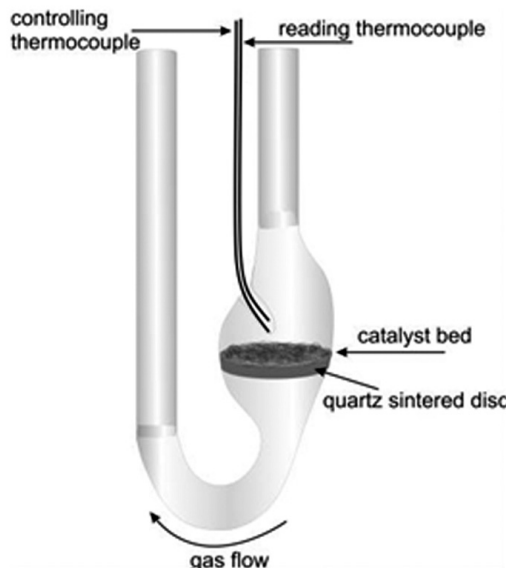


Fig. 2. The quartz reactor for catalytic measurements

The catalyst in the form of a sieve fraction (0.2–0.3 mm or similar) is placed on the quartz sintered disc inside the reactor in an amount corresponding to a thin layer of catalyst grains (~300 mg). It should be noted that, in order to obtain fast detector response, the volume between the catalyst bed and Quadrupole Mass Spectrometer (QMS) capillary should be minimized.

Catalytic test procedure

Catalytic tests are performed in a temperature programmed mode. A constant feed of the reactants, flow rate $30 \text{ ml} \cdot \text{min}^{-1}$, is supplied to the reactor. The temperature of the reactor, which is placed in an electronically controlled furnace, is raised gradually with a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$. The temperature of the reactor is recorded and gas phase composition is monitored by means of the QMS. The mass spectrometer is operated in a “*p* vs. *t*” mode, which means that the selected *m/z* ratios are recorded continuously with time. The signals of *m/z* = 44 (N_2O , CO_2), 32 (O_2), 30 (NO), 28 (N_2 , CO) and 18 (H_2O) are recorded. From the signal *m/z* = 44 the conversion of N_2O is calculated. Prior to each experiment, the water and carbonate species should be removed from the catalyst surface as they severely affect the rate of the reaction. This is achieved by heating the catalyst sample in an inert gas up to the temperature where the signal from *m/z* = 18 and 44 decays (873 K).

Nitrogen(I) oxide decomposition can be regarded as the 1st order reaction with respect to N₂O (Kapteijn et al., 1996), according to the equation:

$$r = k^{app} \frac{P_{N_2O}}{p^0} \quad (4)$$

With the material mass balance for a mixed flow reactor, the equation can be obtained combining the N₂O conversion with the activation energy and temperature. In Appendix A the development of the model is presented. Eventually, through nonlinear fitting of A' and E_a to the model, Eq. (5), for a given set of T and X (preferably for conversions lower than 30%), the activation energy, E_a , can be estimated:

$$X = \frac{A' e^{\frac{-E_a}{RT}}}{1 + A' e^{\frac{-E_a}{RT}}} \quad (5)$$

where: r (s⁻¹) – the surface reaction rate; k^{app} (s⁻¹) – the apparent reaction rate constant; p_{N_2O} (Pa) – N₂O partial pressure (the same units as total pressure); p^0 (Pa) – the total pressure; E_a (kJ·mol⁻¹) – the apparent activation energy of N₂O decomposition (units depend on the gas constant); A' (s⁻¹) – the generalized prefactor in the Arrhenius equation (Appendix A)

Work function measurements

The Kelvin method is based on the occurrence of a contact potential difference (V_{CPD}) between the surfaces of two different materials (electrodes) which are electrically connected, these being the Kelvin probe (p) and the sample under investigation (s) (Nonnenmacher et al., 1991). These are placed close to each other to form a capacitor, which collects the related surface charge. The appearance of this contact potential difference is a result of the different energy of Fermi levels of the unconnected Kelvin probe and the sample. At the time of connection, the Fermi level of the system is equating. The electrons from the higher Fermi level material are moving to the other material's conduction band until the same electrochemical potential is reached in both of them. This movement of charges brings about a contact potential difference between the electrodes.

The contact potential difference (V_{CPD}) measurements were carried out by the dynamic condenser method of Kelvin with a KP6500 probe (McAllister Technical Services) under a dynamic vacuum of the order 10⁻²-10⁻³ mbar. For the work function measurements, the samples (about 150 mg) were pressed into the pellets (10 mm in diameter) under a total pressure of 8 tons. To standardize the surface, the samples were heated at 673 K for 15 min and the V_{CPD} measurements were carried out at 423 K. Because work function measurement is very sensitive, its results can be influenced by weather conditions. For

that reason it is advised to perform the whole series of measurements on the same day. The V_{CPD} values are converted into the work function with the use of the simple relation $eV_{\text{CPD}} = \Phi_{\text{ref}} - \Phi_{\text{sample}}$.

Results

The effect of adsorbed potassium on the catalytic activity (the energy of activation) and the work function of cobalt spinel was observed. Results obtained for K-doped commercial spinel (Fluka) with measured surface $16 \text{ m}^2 \cdot \text{g}^{-1}$ are presented in Fig. 3.

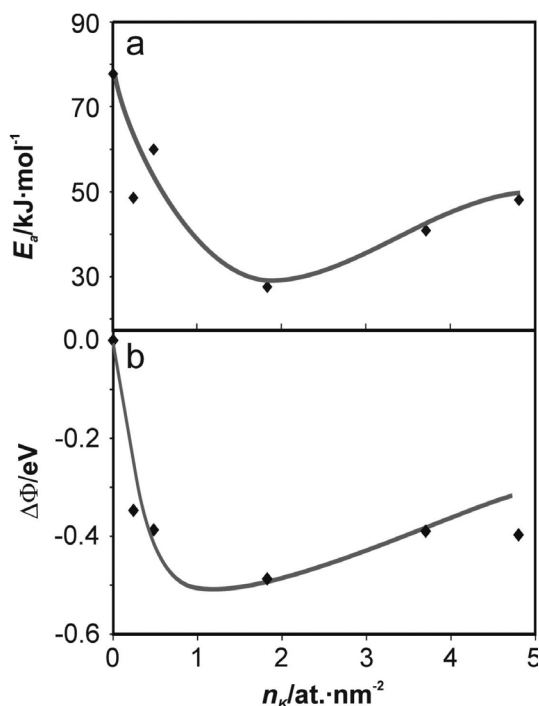


Fig. 3. Dependence of a) activation energy (E_a) of N_2O decomposition and b) work function changes of the catalyst on potassium loading (Zasada et al., 2009)

The linear drop in the work function, at low surface loading, is a result of forming potassium positive ions and creating surface dipoles. The increase in potassium coverage leads to a mutual depolarization and, after passing the minimum, the work function starts to increase with the amount of potassium added. The resultant non-monotonous character of the work function changes can be analyzed on the basis of the Topping equation (Brison et al., 2007):

$$\Delta\Phi = -\frac{\mu}{\varepsilon_0} \cdot n_K \cdot \left(1 + \frac{\kappa \cdot \alpha \cdot n_K^{3/2}}{4 \cdot \pi \cdot \varepsilon_0} \right)^{-1} \quad (6)$$

where: $\Delta\Phi$ is expressed in eV, n_K in m^{-2} , and $\kappa\alpha$ expressed in $\text{C}\cdot\text{m}^2/\text{V}$ is the product of the geometrical factor and polarizability of surface potassium. The κ value varies from 9 - 11 depending on the surface packing which implies that the value of polarizability of surface potassium is in the range $\alpha = 17 - 27 \text{ \AA}^3$, in line with the literature data (Verhoef & Asscher, 1997).

Then experimental data, $\Delta\Phi$ versus n_K , can be fitted with the Topping model and the surface dipole moment μ can be determined. The curves were fitted with the use of the nonlinear fit function implemented in the Mathematica software. However, it can be done with the use of other available software such as OriginLab or Solver functionality in MS Excel. The minimum doping range to obtain results that can be analysed with the Topping model is 0-5.

Hazards

Cobalt(II,III) oxide may cause irritation to the skin, eyes and respiratory tract. It is harmful if swallowed. Exposure to nitrogen(I) oxide by inhalation can cause euphoria, drowsiness and unconsciousness. Vacuum measurements should be made under the supervision of a trained instructor.

The experiment overview

The experiment can be introduced not only to chemistry students, who are specialising in catalysis, but also to material engineering students, who will be interested in the design and tuning of new materials and surface properties. The experiment can be completed in 20 laboratory hours, exemplary time balance is presented in Table 1. Part 2 and 3 of the experiment can be carried out simultaneously. Students should share duties for the most effective use of time. Based on experience, it can be concluded that the time needed for consultations with a tutor for one group is 3 - 5 h. Studying the literature and preparation of the final report (internal publication) ~ 10 h per group. The main investigation can be preceded by spinel synthesis and studies of the surface area in dependence on calcination conditions. Additionally, fitting the Topping curve can be the task of a separate computer laboratory (Brison et al., 2007).

Evaluation of the experiment

Methodology and research group

An evaluation of the experiment was based on questionnaire survey followed by short interview. In the questionnaire "Plus, Minus, Interesting tool" (PMI) (De Bono,

Table 1. The experimental time load

Part	Action	Time
Preparation	Preparation of sieve fraction of un-doped cobalt spinel.	1 h
	Preparation of K_2CO_3 solutions. Potassium impregnation of cobalt spinel (5 samples).	2 h
	Calcination of the prepared potassium-doped cobalt spinel sample.	1 h
Work function measurement	Preparation of cobalt spinel pellets.	1 h
	Work function measurements.	5 h
Activity tests	Catalytic tests.	2 h/sample Total 10h

2005) was used. The PMI tool is used to see many perspectives on an argument or event and think more broadly about an issue. It is usually used as a simple decision making tool, but in this case it was used to open up responder's thinking and encourage creativity. In the next part of the survey students had to assess parts of the experiment (planning, experimental part, report) - its difficulty and load of work that was necessary to complete. Assessment was based on five-point Likert (1932) scale: 1 – very easy, 2 – easy, 3 – medium, 4 – hard and 5 – very hard. The questionnaire was followed by a short interview during which students answered two questions: 'What have you learned during the experiment?', 'Do you think knowledge and skills you gathered during the experiment were useful?'

So far, the experiment was attended by three groups with 4 students in each. The evaluation survey and the interview were fulfilled by 9 participants. The evaluation was conducted 6-12 months after completion of the course. The interview part was performed with each of the respondents separately.

Results

The three most frequent answers in each part of PMI tool are shown below. In the bracket the frequency of answers is given.

Most frequent 'Pluses':

Autonomy during research (x6)

Flexible working hours (x5)

The involvement of assistants (x4)

Most frequent 'Minuses':

Lack of equal sharing of responsibilities (x4)

I couldn't participate in every part of the experiment (x3)

Group was too large (x2)

Most frequent 'Interesting':

Topic related to environment protection (x5)

Experiment based on real/autonomic research (x4)

Topic related to catalysis (x2)

Results of the assessment of the difficulty and load of work that was necessary to complete experimental parts are presented in the Table 2. The most frequent answer (mode) is shown with its frequency. Additionally, median and arithmetic average are presented.

Table 2. Results of the evaluation of the difficulty and load of work, necessary to complete the experiment, assessed using five point Likert scale (1 – very easy to 5 – very hard)

Assessed part		Mode	Mode freq.	Median	Average
Difficulty	Planning	3	7	3	3,00
	Experiment	3	6	3	2,89
	Report	4	4	3	3,22
Load Of Work	Planning	3	6	3	3,11
	Experiment	4	7	4	3,78
	Report	4	6	4	3,67

The results of an interview part are presented in the same manner as the PMI tool, the most frequent answers with its frequency are given below.

What have you learned during the experiment? Answers:

Using Kelvin probe and reactivity tests (including interpretation of results) (x6)

Making pellets (x4)

Writing (the report) in the form of publication (x3)

Do you think knowledge and skills you gathered during the experiment were useful?

Eight of nine responders answered 'Yes', and further:

For the Bachelor thesis (for research and writing) (x5)

During other courses (x3)

While writing own publication (x1)

Discussion of the experiment evaluation

Results of the ‘Plusses and Minuses’ part of the PMI tool show that students’ remarks concern mainly to organisation of the course, not to the scientific content. The answers related to subject of the experiment appear in the ‘Interesting’ part. Analysis of ‘Plusses’ and ‘Minuses’ statements show that students are satisfied with the possibility of making research-based investigation with high autonomy but they have a major problem with working in groups. Observation of students laboratory work shows that almost every student tried to participate in each part of the research personally, what was sometimes hard to complete due to different set other courses chosen by them. Also, none of the groups chose one of the participants to be a leader/manager of the study, they tried to manage and make decisions collectively. This can be the reason why groups with 4 people were considered by students as too large. The PMI tool results give quite interesting view of the experiment realization, and allow identifying the most problematic issues.

The easiest and least demanding part was indicated to be the planning, graded with average marks in both areas. The experimental part was considered as moderately difficult but more laborious. As the most challenging part the reporting was marked which was assessed as difficult with significant amount of time and work required to complete. These results are not surprising, since the experimental report has to be presented in form of scientific publication. For most of the students it’s the first attempt to present result in this form. On the other hand, skills gained during this part were most frequently mentioned in the interview part as answer to question ‘Do you think knowledge and skills you gathered during the experiment were useful?’

The part of the interview in which students were asked to say ‘What have you learned during the experiment?’ shows that students are convinced that they have learned to use a Kelvin probe and perform reactivity tests with interpretation of results. Surprisingly, as small and specific skill as ‘Making pellets’ was considered as one of the skills they gained during the experiment. This probably results from fact that this action was repetitive and every student had the opportunity to complete it several times.

Conclusions

The presented experiment demonstrates tuning of the electronic properties of the catalyst by surface doping with alkali. The described study should be treated as a base for modification. In individual approach the research questions with currently unknown answers should be chosen, so the experiment could be real research-based laboratory experience. Regardless of the studied aspect, the experiment offers a good opportunity to familiarize students with the catalytic test procedure and the determination of the work function of the material.

The results of the evaluation of the experiment provide information about the content of the experiment and more general about the impact of research-based laboratory. It can be stated that the experiment was assessed as moderately difficult, and the hardest part was the reporting. Results show students' self-confidence in planning the investigation and performing research tasks. The biggest challenge for students is the independent organization of the group work. Students seem to have troubles in task management and decision making. This aspect will be investigated in details in next iteration of the experiment and its evaluation.

APPENDIX A: DETERMINATION OF KINETIC PARAMETERES

List of symbols

$F_{N_2O}^0$ (s^{-1}) – molecular flow rate of input N_2O

F_{N_2O} (s^{-1}) – molecular flow rate of output N_2O

V (m^3) – reacting volume

r_v ($s^{-1} \cdot m^{-3}$) – reaction rate, amount of N_2O produced by reaction, product of reaction rate and stoichiometric number (–1 for N_2O)

r (s^{-1}) – surface reaction rate

$m_{cat}/(g)$ – catalyst mass

S ($m^2 g^{-1}$) – catalyst specific surface area

ρ (m^{-2}) – active centres concentration

F^0 (s^{-1}) – molecular flow rate of input mixture

$\tau = \frac{m_{cat} S \rho}{F^0}$ (s) – can be regarded as the time in which the number of molecules passing from the gas mixture through the reactor equal the number of active centres on the catalyst surface

$x_{N_2O}^0$ – N_2O molar fraction at the input

x_{N_2O} – N_2O molar fraction at the output

p^0 (Pa) – total pressure

p_{N_2O} (Pa) – N_2O partial pressure (the same units as total pressure)

A (s^{-1}) – prefactor in the Arrhenius equation

E_a ($kJ \cdot mol^{-1}$) – apparent activation energy of N_2O decomposition (units depend on gas constant)

k^{app} (s^{-1}) – apparent reaction rate constant

The model of catalytic reactor

For a flow reactor with a perfect mixing of reactants (model of mixed flow reactor), in a steady state, the material mass balance can be written as:

$$F_{N_2O}^0 = F_{N_2O} + (r_V)V \quad (A1)$$

The observed reaction rate in volume V is given by the product of r_V and V , which for heterogeneous process is equal to the rate of surface reaction. Thus:

$$r_V V = r m_{cat} S \rho \quad (A2)$$

With the definition of the conversion of N_2O in form $X = \frac{F_{N_2O}^0 - F_{N_2O}}{F_{N_2O}^0} = \frac{x_{N_2O}^0 - x_{N_2O}}{x_{N_2O}^0}$ we obtain $F_{N_2O} = F_{N_2O}^0(1 - X)$ and Eq. (A2) can be rewritten in form:

$$r m_{cat} S \rho = F_{N_2O}^0 X \quad (A3)$$

Molecular flow of N_2O is given by $F_{N_2O}^0 = F^0 x_{N_2O}$, thus

$$r = \frac{F^0}{m_{cat} S \rho} x_{N_2O}^0 X \quad (A4)$$

and

$$r = \frac{x_{N_2O}^0 X}{\tau} \quad (A5)$$

For the apparent first order reaction, such as N_2O decomposition (for $\frac{P_{N_2O}}{P^0} = x_{N_2O}$), the rate is expressed as $r = k^{app} x_{N_2O} = k^{app} x_{N_2O}^0(1 - X)$ and combining with Eq. (A5) we obtain

$$k^{app} \cdot \tau = \frac{X}{(1 - X)} \quad (A6)$$

or

$$X = \frac{\tau k^{app}}{1 + \tau k^{app}} \quad (A7)$$

$$r = \frac{x_{N_2O}^0}{\tau} \frac{\tau k^{app}}{1 + \tau k^{app}} = x_{N_2O}^0 \frac{k^{app}}{1 + \tau k^{app}} \quad (A8)$$

After substitution into Eq. (A8) reaction rate constant expressed as Arrhenius dependence (Eq. (A9)) one can determine the apparent activation energy from conversion

and temperature from the experiment (Eq. A(10)) with the use of mathematical software and a nonlinear fitting procedure (e.g. Mathematica, OriginLab).

$$k^{app} = A e^{\frac{-E_a}{RT}} \quad (A9)$$

$$X = \frac{\tau A e^{\frac{-E_a}{RT}}}{1 + \tau A e^{\frac{-E_a}{RT}}} \quad (A10)$$

In this model, the activation energy is independent of the amount of catalyst used, its specific surface area and concentration of surface active centres. Thus, τ can be incorporated in the prefactor A obtaining $A' = \tau A$.

For a plug flow reactor model the apparent reaction rate constant is expressed according to Eq. (A11), and the expression combining the activation energy is obtained by combining with Eq. (A9).

$$k^{app} = \frac{1}{\tau} \ln \frac{1}{1-X} \quad (A11)$$

REFERENCES

- Bredow, T., Aprà, E., Catti, M. & Pacchioni, G. (1998). Cluster and periodic ab-initio calculations on K/TiO₂(110). *Surf. Sci.*, 418, 150 – 165.
- Breedon, M., Spencer, M.J.S. & Yarovsky, I. (2009). Adsorption of NO and NO₂ on the ZnO(2110) surface: A DFT study. *Surf. Sci.*, 603, 3389 – 3399.
- Brisson, J., Mine, N., Poisseroux, S., Douhard, B., Vitchev, R.G. & Houssiau, L. (2007). Measurement and modeling of work function changes during low energy cesium sputtering. *Surf. Sci.*, 601, 1467 – 1472.
- Brownell, S.E., Kloser, M.J., Fukami, T. & Shavelson, R. (2012). Undergraduate biology lab courses: comparing the impact of traditionally based ‘cookbook’ and authentic research-based courses on student lab experiences. *J. College Sci. Teaching*, 41, 36 – 45.
- Davis, M.E. & Davis, R.J. (2003). *Fundamentals of chemical reaction engineering*. New York: McGraw-Hill.
- De Bono, E. (2005). *De Bono's thinking course*. Portland: Barnes & Noble.
- El-Shobaky, H.G. & Turkey, A.E.M. (2002). Effect of gamma-irradiation on surface and catalytic properties of Co₃O₄ and NiO catalysts. *J. Radioanal. & Nuclear Chem.*, 254, 151 – 158.

- Fischer, J.E. (2003). Spectroscopic monitoring of the heterogeneous catalytic decomposition of gaseous ammonia. *J. Chem. Educ.*, 80, 1451 – 1454.
- Huang, W., Lai, W. & Xie, D. (2008). First-principles study of decomposition of NH_3 on Ir(100). *Surf. Sci.*, 602, 1288 – 1294.
- Kapteijn, F., Rodriguez-Mirasol, J., Moulijn, J.A. (1996). Heterogeneous catalytic decomposition of nitrous oxide. *Applied Catalysis B: Environmental*, 9, 25 – 64.
- Kotarba, A., Adamski, G., Piskorz, W., Sojka, Z., Sayag, C. & Djéga-Mariadassou, D. (2004). Modification of electronic properties of Mo_2C catalyst by potassium doping: impact on the reactivity in hydrodenitrogenation reaction of indole. *J. Phys. Chem. B*, 108, 2885 – 2892.
- Laursen, A. (2011). The Sabatier principle illustrated by catalytic H_2O_2 decomposition on metal surfaces. *J. Chem. Educ.*, 88, 1711 – 1715.
- Likert, R. (1932). A technique for the measurement of attitudes. *Arch. Psychol.*, 140, 5 – 55.
- Mattson, B. (2006). Propanol to propane: an advanced laboratory experiment using heterogeneous catalysts for two successive gas-phase reactions. *J. Chem. Educ.*, 83, 421 – 424.
- Moura, F. (2006). Experiments on heterogeneous catalysis using a simple gas chromatograph. *J. Chem. Educ.*, 83, 417 – 420.
- Nonnenmacher, M.M., O’Boyle, M.P., & Wickramasinghe, H.K. (1991). Kelvin probe force microscopy. *Appl. Phys. Lett.*, 58, 2921 – 2926.
- Okumura, M.L. (1996). Undergraduate laboratory for surface science (NSF). *J. Chem. Educ.*, 73, 142.
- Parmon, V.N., Panov, G.I., Uriarte, A. & Noskov, A.S. (2005). Nitrous oxide in oxidation chemistry and catalysis: application and production. *Catalysis Today*, 100, 115 – 131.
- Pérez-Ramírez, J., Kapteijn, F., Schöffel, K. & Moulijn, J.A. (2003). Formation and control of N_2O in nitric acid production: where do we stand today. *Applied Catalysis B: Environmental*, 44, 117 – 151.
- Pietrzyk, P., Zasada, F., Piskorz, W., Kotarba, A. & Sojka, Z. (2007). Computational spectroscopy and DFT investigations into nitrogen and oxygen bond breaking and bond making processes in model deNO_x and deN₂O reactions. *Catalysis Today*, 119, 219 – 227.
- Piskorz, W., Zasada, F., Stelmachowski, P., Kotarba, A. & Sojka, Z. (2008). Decomposition of N_2O over the surface of cobalt spinel: a DFT account of reactivity experiments. *Catalysis Today*, 137, 418 – 422.
- Raymundo-Pinero, E.D. (1999). Catalytic oxidation of sulfur dioxide by activated carbon. *J. Chem. Educ.*, 76, 958.

- Roman, T. & Groß, A. (2013). Periodic density-functional calculations on work-function change induced by adsorption of halogens on Cu(111). *Phys. Rev. Lett.*, 110, art. no. 156804.
- Sensato, F.R., Custódio, R., Calatayud, M., Beltrán, A., Andrés, J., Sambrano, J.R. & Longo, E. (2002). Periodic study on the structural and electronic properties of bulk, oxidized and reduced SnO₂(110) surfaces and the interaction with O₂. *Surf. Sci.*, 511, 408 – 420.
- Somorjai, G.A. (1994). *Introduction to surface chemistry and catalysis*. New York: Wiley.
- Stelmachowski, P., Maniak, G., Kotarba, A. & Sojka, Z. (2009). Strong electronic promotion of Co₃O₄ towards N₂O decomposition by surface alkali dopants. *Catalysis Commun.*, 10, 1062 – 1065.
- Verhoef, R.W. & Asscher, M. (1997). The work function of adsorbed alkalis on metals revisited: a coverage-dependent polarizability approach. *Surf. Sci.*, 391, 11 – 18.
- Young, M.A. (2009). Real-time monitoring of heterogeneous catalysis with mass spectrometry. *J. Chem. Educ.*, 86, 1082 – 1084.
- Zasada, F., Kotarba, A., Sojka, Z., Paul, J., Stelmachowski, P. & Maniak, G. (2009). Potassium promotion of cobalt spinel catalyst for N₂O decomposition-accounted by work function measurements and DFT modelling. *Catalysis Letters*, 127, 126 – 131.

✉ **Dr. Pawel Bernard (corresponding author)**

Department of Chemical Education
Jagiellonian University
30-060 Krakow, Poland
E-mail: pawel.bernard@uj.edu.pl

Dr. Gabriela Grzybek

Dr. Pawel Stelmachowski
Materials and Surface Chemistry Group,
Department of Inorganic Chemistry,
Jagiellonian University
30-060 Krakow, Poland