Application of h-BN Nanomesh in Molecular Adsorption and Metal-Catalyzed Processes

Theses of the doctoral (Ph. D.) dissertation

Szitás Ádám

Supervisors:

Prof. Dr. Kónya Zoltán

Full professor

Dr. Farkas Arnold Péter

Research fellow

University of Szeged

Applied and Environmental Chemistry Department

Doctoral School of Chemistry

2021

I. Introduction, objectives

In the second half of the twentieth century, the general approach to the chemical industry changed significantly. In addition to the large-scale production of products, the importance of selectivity, the need for predictability in the number and quantity of by-products and the impact of the given technology on the environment also came to the fore. As a result, there has been an expectation of a thorough understanding of the various chemical processes in order to make chemical processes as controllable and designable as possible. One of the directions of the research methodology is the so-called bottom-up technique, where we build more complex, multi-component systems based on pure single crystals under ultra-vacuum conditions. The advantage of the bottom-up method is that the processes taking place in the examined system are easier to understand at the elementary level and based on the experience and results gained in this way, multi-component, complex practical systems, e.g. the design of automotive or industrial catalysts can become smoother and simpler. In order to meet the above expectations, researchers are also making a special effort to study increasingly modern, increasingly special materials. This is also necessary because it is often justified to use very complex and special systems that have unique physical-chemical properties and try to meet several needs at the same time. One such special system is the family of two-dimensional materials. 2D materials came to the forefront of researchers interest after the discovery of graphene (an atomic layer of graphite). The boron nitride analog of graphene, hexagonal boron nitride (h-BN), contains alternating boron and nitrogen atoms and shares several favourable physical and chemical properties with graphene. During my doctoral research, I became involved in the work of the MTA-SZTE Reaction Kinetics and Surface Science Chemistry research group, where I dealt with the adsorption properties of h-BN; on the one hand, the metal-catalyzed processes of ethanol and acetaldehyde were investigated, and on the other hand, its use as a molecular adsorption template on this surface was studied. The support of the produced h-BN layer, the substrate we used, was a (111) Miller-index rhodium single crystal (Rh(111)). Small organic molecules such as ethanol and acetaldehyde were studied on the surface of pure and various modified rhodium single crystals. In this case, we take advantage of the property of the h-BN monolayer that, when synthesized on single crystals with (111) Miller-indices, a regular structure is formed (edge-pores), and the resulting structure is characterized by periodic corrosion. The diameter of the pores thus formed (~2 nm) coincides with the size range in which gold is

catalytically active. Our aim is to understand and describe in detail the possible reaction pathways on pure Rh(111) and modified single crystal surfaces for the molecules. In the modifications we applied, we created an atomic layer-thick h-BN nanomesh on the surface of the Rh single crystal on which Au nanoparticles were prepared.

We also examined larger molecules, e.g. cyclohexene, benzene, azobenzene, adsorption properties. In this case, we took advantage of the property of the h-BN monolayer that the regular, ordered nanomesh structure on the Rh(111) single crystal surface was generally considered inert. Based on this, the interaction between the electrically conductive support (Rh single crystal) and the molecule to be tested is presumably minimized - in fact, the nanomesh acts as an insulator, allowing the adsorption properties of molecules to be studied in a much more inert environment we can perform measurements e.g. formation of molecular coupling reactions or heterogeneous nanostructures (heterostructures). Our objectives included the creation of an h-BN / carbon-based heterostructure on the Rh(111) surface. We planned to implement our experiments in two directions depending on the circumstances: first on the surface of the intact h-BN, without its decomposition and on the other hand to form the carbon (e.g. graphene) layer (graphene / h-BN / Rh(111))) in a 2D lateral structure where carbon is incorporated into the nanomesh structure of h-BN (graphene-h-BN / Rh(111)).

II. Experimental methods

The most important experimental methods used in my doctoral work were high-resolution electron energy loss spectroscopy (HREELS), temperature-programmed desorption (TPD) and Auger-electron spectroscopy (AES). In addition, in evaluating my results, I relied on the experimental (STM, XPS) and theoretical (DFT) work of my colleagues, who also performed measurements on these or similar systems. The method we use most is high-resolution electron energy loss spectroscopy (HREELS), a surface-sensitive electron spectroscopic method for studying processes on surfaces with long-term ordering. During its application, the interaction of the solid sample and the low-energy (~ 1-10 eV) monochromatic electron beam focused on its surface is investigated, where the primary electron beam is provided by a low-energy electron gun. The electrons leaving the filament (filament made of lanthanum hexaboride, LaB_6) reach the sample through a monochromator where vibrational excitation takes place; then, the energy-lost electrons reflected from the surface are detected by an electron energy analyzer of a structure similar to that of a monochromator. The excitation levels of the particles adsorbed on the surface of the sample are also involved in the process, so the method is suitable for studying the adsorbed particles. The HREELS method provides information on the vibrational transition of adsorbed molecules. Its advantage is that all modes of vibration (infrared as well as Raman-active and optically inactive modes) can be observed in the spectrum. Electrons with an initial energy E_i arriving at the surface of the sample generate scattered (primary) and emitted (secondary) electrons. It also depends on the primary energy of the electrons and the geometry of the measurement which of the possible interactions is dominant. In dipole scattering, the primary electron interacts with dipoles on the surface through a long-term Coulomb force (e.g. molecular vibration). Approaching the surface, the electron creates an electric field that induces a mirror charge on the surface of the sample. This oscillating force field is perpendicular to the surface and can only excite vibrations for which the change in dipole moment is also perpendicular to the surface (or there is a component perpendicular to the surface). For metal surfaces, two more selection rules come to the fore. According to the first, only vibrations perpendicular to the surface are active in HREELS. The second selection rule states that the intensity has a maximum when the angle of reflection is equal to the angle of incidence (specular geometry). The scattering electron loses energy and then leaves the sample in a specular direction. By specular geometry is meant when both the incident

and scattered electron beams form an angle of 60° with the normal of the surface. Impact scattering occurs during a short-term interaction between a particle on a surface and an impacting electron. Exact description of these processes is possible by quantum mechanical methods. During the collision, the electrons are scattered over a wide spatial angle range, in which case the detection is performed at a so-called 45-50° angle with the surface normal performed in an off-specular arrangement. It is important to note that electrons generated by the collisional scattering mechanism can also be measured while using a detection geometry different from the 60° detection angle mentioned above (typically 10-20°), in contrast to electrons generated by the dipolar scattering mechanism, which already have small deviations (a few degrees) also give a signal of reduced intensity.

Auger electron spectroscopy (AES) is a widely used method for studying the chemical composition of solid surfaces. It is also an analytical electron emission spectroscopic technique suitable for elemental composition analysis. It is based on the Auger effect, according to which incident electrons with an energy of 3-5 keV from the primary electron beam eject electrons from the inner electron shells of atoms on the surface of the sample. An electron from a higher energy level than the original can replace the resulting deficit and the released energy is an electron on a third shell, the so-called Auger electron. Auger electrons are electrons with characteristic kinetic energy generated during the ionization of atoms in the solid. Examining the energy of the outgoing electron, we can get information about the environment (composition and structure of the surface) in which the Auger process took place, i.e. the energy of the outgoing electron carries the desired information.

The equipment used for our measurements (BALZERS, Prisma) is a heated cathode mass spectrometer with a four-pole (quadrupole) analyzer in terms of separation. The electrons exiting the heated filament split and ionize the molecules in the gas space into fragments. These fragments are selected by the analyzer by mass / charge (m / z) so that they can be analyzed. The analyzer contains two cylindrical electrodes arranged in parallel, one of which is opposite each other in time, while the other creates a variable electric field. By changing the field strength, you can control which fragments reach the sensitive space of the detector, the detector is an electron multiplier. Mass spectrometry can be used to support and supplement measurements performed with temperature-programmed desorption (TPD) techniques. In our case, the sample is heated with a tantalum (Ta) heating wire at a specified speed while the temperature is measured with a thermocouple

and the intensity of the mass spectrometer signal is detected at the given m / z using the MS device. The amount of desorbed gases as a function of temperature is measured by turning the sample towards the mass spectrometer. Thus, we can obtain both quantitative and qualitative information using TPD technique. Our experiments were performed under ultrapure conditions in a two-level ultra-vacuum chamber made of stainless and acid-resistant steel. The vacuum chamber can be technically divided into two parts. The first part, a smaller volume gas-inlet system, to which are connected the gas cylinders, containers, which contain the substances to be adsorbed on the surface of the sample. A rotary and a turbomolecular pump controlled the pressure in this space, and the pressure here was measured with a Pirani vacuum gauge. Vacuum is generated in a similar way for the second space (main chamber); the main chamber contains the major spectroscopic equipment. Here, the typical pressure before starting work was typically $\sim 5 \times 10^{-10}$ mbar (incandescent cathode ionization vacuum gauge), which was achieved using turbomolecular and oil rotation pumps. The pre-vacuum space was connected to the UHV chamber through a 0.1 mm diameter capillary, and the sample was placed at a distance of ~3 cm from the capillary during the exposure. The sample was attached to a tantalum sample holder in direct contact with a copper container through which liquid nitrogen was cooled to 160 K by the addition of liquid nitrogen. Heating was accomplished with Ta heating wire attached to the sample and bent as a heating wire behind the sample. With this method we were able to reach a maximum temperature of ~1100 K, which was measured with a spot-welded thermocouple for the sample. The sample holder can be moved in three directions (x, y, z) of the space, connected to a manipulator (φ) that can be rotated almost 360° along its vertical axis. This allowed accurate and precise positioning of the sample in the main chamber after determining the appropriate (x, y, z φ) coordinates. The purity of the Rh(111) single crystal surface was achieved by alternating argon ion bombardment, oxidation, and high temperature thermal treatments. Evaporation of the metals to be studied was performed with a four-position PVD source (manufactured by Oxford Applied Research) designed for this purpose. High purity metals (99.95%) were placed in a carbon sample crucible (for lower melting point metals) or captured in the appropriate position in the evaporator in the form of a metal rod.

III. New Scientific Results

1. The adsorption of acetaldehyde was investigated on the surface of pure and carbon-covered Rh(111) single crystal in a wide temperature range (170–1000 K). Processes on the surface of the Rh(111) single crystal sample were followed by HREELS and TPD methods.

T1.1 HREELS measurements confirmed that the adsorption of acetaldehyde leads to the formation of oligomers (dimer and trimer forms) on the pure Rh(111) single crystal surface at low temperature (170 K). η^1-(O)-CH$_3$CHO$_a$ and η^2-(O, C)-CH$_3$CHO$_a$ forms were identified on the surface. We have shown that the form of η^1-(O)-CH$_3$CHO$_a$ is the one that is organized into a dimer, trimer, or 2D polymeric form. TPD measurements confirmed that the residual acetaldehyde is partially desorbed and partly dissociated CO, H$_2$ and CH$_4$ products upon surface heating.

T1.2 HREELS and TPD methods proved that modification of the pure Rh(111) surface with carbon layer, even at low C coverage (θ_C = ~0.05), the acetaldehyde polymerization process is reduced due to the lack of appropriate adsorption centres and active sites. Furthermore, we have already registered the cleavage of the carbon-oxygen bond of acetaldehyde at 230 K on the carbon-modified Rh(111) surface (on the pure surface it is around 300 K) together with the formation of carbon monoxide bound at three-fold hollow sites.

T1.3 The stabilizing effect of small amounts of surface carbon on the desorption products of acetaldehyde (H$_2$ or CH$_4$) has been demonstrated by TPD measurements. The desorption products were analyzed at higher temperatures (430 or 300 K) compared to the pure Rh(111) surface (400 or 270 K). However, the TPD peak maxima of the CO desorption does not follow the observed trend at hydrogen and methane, but its desorption temperature reduces because CO molecules can only bind to less stable sites due to surface carbon content.

2. Gold was evaporated by the method of physical vapor deposition on the surface of a pure and h-BN monolayer covered Rh(111) single crystal sample surface. The adsorption properties and catalytic processes of acetaldehyde were investigated on the surface of the samples. The aim of the applied modifications is to study the catalytic reaction pathways of acetaldehyde over nanoscale gold clusters in an isolated environment with the help of h-BN monolayer on Rh(111).

T2.1 HREELS and TPD results showed that in the absence of appropriate active centers, the polymerization process of acetaldehyde is repressed. This is because a strong interaction between the acetaldehyde molecule and the substrate Rh single crystal is required to play this process, which requires the presence of pure Rh terraces (due to the gold coverage, the number of these sites decreases). The presence of oligomers has previously been detected in a sample surface rich in such pure Rh terraces.

T2.2 With our HREELS measurement results we proved that the amount of CO from acetaldehyde dissociation on pure rhodium decreases on the ordered 2×1 Au-Rh surface alloy. This is due to the lack of suitable active centres, so there is no suitable situation to play the decomposition of acetaldehyde.

T2.3 TPD results showed that the h-BN / Rh(111) system can increase the stability of acetaldehyde on the boron nitride surface with the help of evaporated gold. The amount of adsorbed acetaldehyde can be increased up to ~2 ML gold coverage, while the number of edge and corner (low coordinated) Au atoms also increases in the formed Au nanoclusters.

3. We studied the reactivity of ethanol on the surface of pure and gold-decorated h-BN monolayer formed on the surface of Rh(111) single crystal.

T3.1 HREELS and TPD results demonstrated that the Au / h-BN / Rh(111) system can be used in the ethanol dehydrogenation reaction. According to our measurements, our model catalyst is the most active in the case of a privileged Au coverage (~1.5 ML). The coverage range is found to be best for ethanol conversion when the most edge and corner (low-coordinated) Au atoms take place at the surface when the Au / h-BN interface is the largest. Our measurements confirmed that the h-BN nanomesh not only serves as an excellent carrier for Au nanoclusters, but it also acts as an active partner in the dehydrogenation process, which is supported by the appearance of the peak ν(B-H) = 2660 cm^{-1} according to HREELS results.

T3.2 Using HREELS technique, we showed that the Rh(111) single crystal surface covered with the h-BN monolayer cannot promote the cleavage of the C-C bond because there is no suitable active centre on the Au / h-BN / Rh(111) system for that. Hydrogen was produced selectively without CO formation. TPD and HREELS measurements confirmed that acetaldehyde and molecular hydrogen are the main desorption products. We determined a preferred gold coverage range (at and around 1.5 ML) when the amount of products reached a maximum.

4. We studied the adsorption properties of azobenzene, benzene and cyclohexene on the h-BN / Rh(111) system, in order to understand the behaviour of the h-BN nanomesh formed on the Rh(111) single crystal in molecular adsorption processes and its applicability as a molecular adsorption template.

T4.1 TPD measurements confirmed that azobenzene typically binds to the h-BN / Rh(111) system at two adsorption sites: in the pores and at the wires. We confirmed by angle-dependent HREELS measurements that the vast majority of azobenzene is adsorbed on the surface of the sample as a trans isomer and parallel to the surface, and then desorbs intact with increasing temperature without dissociation.

T4.2 A carbon-boron nitride heterostructure was formed by high temperature (1000 K) adsorption of benzene and cyclohexene on the h-BN / Rh(111) sample. By high-temperature adsorption of benzene, graphene and graphene-like C layers were formed on the surface of the h-BN / Rh(111) sample. However, by high-temperature adsorption of cyclohexene, we were able to create a monolayer carbon-h-BN lateral heterostructure in which the carbon layer was incorporated into the free rhodium "islands" formed by the decomposition of the h-BN monolayer. In other words, the molecule with higher hydrogen content disrupted the continuity of the h-BN layer and, after dissociation, incorporated the carbon into the molecular adsorption template on the surface of the support to form a graphene-like structure.

V. List of Publications

My ID in the Hungarian Collection of Scientific Publications (MTMT) is 10062650.

Journal publications defining the basis of the dissertation

1. Adsorption, polymerization and decomposition of acetaldehyde on clean and carbon-covered Rh(111) surfaces

I Kovács, A P Farkas, <u>Á Szitás</u>, Z Kónya, J Kiss

Surf Sci 664 (**2017**) 129-136

$$IF_{2017}=1,83$$

2. Effect of Gold on the Adsorption Properties of Acetaldehyde on Clean and h-BN Covered Rh(111) Surface

A P Farkas, <u>Á Szitás</u>, G Vári, R Gubó, L Óvári, A Berkó, J Kiss, Z Kónya

Top Catal 61 (**2018**) 1247-1256

$$IF_{2018}=2,32$$

3. Selective transformation of ethanol to acetaldehyde catalyzed by Au/h-BN interface prepared on Rh(111) surface

A P Farkas, <u>Á Szitás</u>, D Jurdi, K Palotás, J Kiss, Z Kónya

Appl Catal A-Gen 592 (**2020**) 117440-117449

$$IF_{2020}=5,01$$

4. Adsorption of Azobenzene on Hexagonal Boron Nitride Nanomesh Supported by Rh(111)

<u>Á Szitás</u>, R Gubó, T Pásztor, A P Farkas, T Ajtai, L Óvári, K Palotás, A Berkó, Z Kónya

J. Phys. Chem. C 124 (**2020**) 14182-14194

$$IF_{2020}=4,19$$

ΣIF=13,35

9

Oral presentations related to the topic of dissertation

1.	Modification of h-BN nanomesh, template for adsorption and catalytic reactions

Á Szitás, A P Farkas, K Palotás, J Kiss, Z Kónya

18th International Conference on Thin Films & 18th Joint Vacuum Conference - Budapest, Hungary 22-26 November 2020

2.	Azobenzol molekuláris kapcsoló adszorpciós tulajdonságainak vizsgálata h-BN nanoháló felületén

Szitás Á, Farkas A P, Óvári L, Palotás K, Berkó A, Gubó R, Pásztor T, Kónya Z

Magyar Fizikus Vándorgyűlés - Sopron, Magyarország 2019. augusztus 21-24.

3.	A. P. Farkas, Á. Szitás, G. Vári, L. Óvári, A. Berkó J. Kiss, Z. Kónya

Effect of gold on the adsorption properties of acetaldehyde on clean and h-BN/Rh(111) surface

European Conference on Surface Science, ECOSS-33, 2017, Aug. 27 – Sept. 1, Szeged

4.	K. Palotás, A. P. Farkas, Á. Szitás, D. Jurdi, R. Gubó, T. Pásztor, L. Óvári, J. Kiss, A. Berkó, Z. Kónya

Comparison of the adsorptions of ethanol and azobenzene molecules on single-layer hexagonal boron nitride on Rh(111)

DPG-Früchjahrstagung, Dresden, 15-20. Marz 2020

5.	Felületi adalékok hatása az acetaldehid reakcióútjaira Rh(111)-en, HREELS és TPD vizsgálatok

Szitás Á, Farkas A P, Kovács I, Kónya Z, Kiss J

Kémiai Előadói Napok - Szeged, Magyarország 2017. október 17.

Poster presentations related to the topic of dissertation

1.   Imre Kovács, Arnold Péter Farkas, <u>Ádám Szitás</u>, Zoltán Kónya, János Kiss, Frigyes Solymosi

Reaction pathways of adsorbed acetaldehyde on the clean and modified Rh(111) surface

European Conference on Surface Science, ECOSS-33, 2017, Aug. 27 - Sept. 1, Szeged

2.   <u>Ádám Szitás</u>, Arnold Péter Farkas, Imre Kovács, Zoltán Kónya, János Kiss

Adsorption, polymerization and decomposition of acetaldehyde on clean and carbon-covared Rh(111) surfaces

European Conference on Surface Science, ECOSS-33, 2017, Aug. 27 - Sept. 1, Szeged

3.   <u>Ádám Szitás</u>, Arnold P Farkas, János Kiss, Zoltán Kónya

Phonon spectra of the clean and metal-modified h-BN monolayer

MPS'18, 21-24 August 2018, Budapest

4.   <u>Ádám Szitás</u>, Arnold P Farkas, Viktória Faur, János Kiss, Zoltán Kónya

Preparation and characterisation of graphene-like carbon layer on h-BN nanomesh

European Conference on Surface Science, ECOSS-34, 26th-31st, August 2018, Aarhus Denmark

5.   <u>Ádám Szitás</u>, Arnold P. Farkas, Viktória Faur, János Kiss, Zoltán Kónya

Preparation and Characterisation of Graphene-like Carbon Layer on h-BN Nanomesh

8th Szeged International Workshop on Advances in Nanoscience (SIWAN-8), 2018. október 7-10. Szeged, Magyarország

6.   Krisztián Palotás, Arnold P Farkas, <u>Ádám Szitás</u>, Dániel Jurdi, Richárd Gubó, Tibor Pásztor, Tibor Ajtai, László Óvári, János Kiss, András Berkó, Zoltán Kónya

Comparison of the adsorptions of ethanol and azobenzene molecules on single-laye hexagonal boron nitride on Rh(111)

Virtual DPG-Frühjahrstagung (DPG Spring Meeting) of the Surface Science Division, 1-4 March 2021

7.   Krisztián Palotás, Arnold Farkas, <u>Ádám Szitás</u>, Dániel Jurdi, Richárd Gubó, Tibor Pásztor, Tibor Ajtai, László Óvári, János Kiss, András Berkó, and Zoltán Kónya

Analysis of ethanol and azobenzene molecular adsorptions on single-layer hexagonal boron nitride on Rh(111)

ICN+T online July 12-15, 2021

Supervisor statements

I declare that the results used in the dissertation of Ádám Szitás doctoral candidate fully reflect the candidate's contribution in the publications serving as the basis of the dissertation.

Prof. Dr. Zoltán Kónya   ……………………………….

    supervisor

Dr. Arnold Péter Farkas   ……………………………….

    supervisor

Szeged, 12th October, 2021