

Investigation of the adsorption properties of cyclic C₆ molecules on h-BN/Rh(111) surface, efforts to cover the boron nitride nanomesh by graphene

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ABSTRACT

The 2D atomic structure of h-BN would be an excellent dielectric layer to complement graphene electronics. When grown sequentially on metal substrates to create GR/h-BN/metal sandwich structures, these nanomaterials can be used in various applications. To this end, in this project we studied the adsorption and dissociation of cyclohexene and benzene on clean and h-BN covered Rh(111) surfaces at low and at high temperatures. Although we observed that both molecules adsorb on the h-BN/Rh(111) surface at 160 K, there is only a weak interaction between these molecules and h-BN. Moreover, h-BN proved to be completely inert to the split of cyclohexene and benzene after low temperature exposures. In our high temperature experiments, we tested the stability of h-BN towards oxygen, hydrogen and we also followed the effects of high exposure adsorption of the C₆ molecules on the nanomesh. We observed a different behavior following the decomposition of the two hydrocarbon species. In one case we developed a graphene-like carbon structure in parallel with BN, while in the other process the carbon layer formed on top of the surface of h-BN/Rh(111). Our results were evidenced by Auger Electron Spectroscopy (AES), High Resolution Electron Energy Loss Spectroscopy (HREELS) and Mass Spectrometry (MS).

1. Introduction

Using boron nitride in graphene-based devices and the combination of the properties of the two materials in multilayer structures can enhance the outstanding features of graphene and open new perspectives, for example in microelectronics. Graphene (GR) and the atomic layers of hexagonal boron nitride (h-BN) are complementary two-dimensional materials with very similar structures, but with vastly different electronic properties. Similarly to graphite, hexagonal boron nitride is a layer material composed of weakly interacting monolayers [1]. The surface structure of h-BN is determined by the strength of interaction with the metal, and it is influenced by lattice mismatch. The h-BN is planar on the close packed surfaces of coinage metals (Cu, Au, Ag, Ni) [1–4]. However on several metals, including Rh(111), the interaction of h-BN is stronger, and a “13 h-BN on 12 Rh” moiré structure is formed: this periodic corrugation is called nanomesh, which has an advantageous template function [5–7]. The new class of boron carbon nitride materials are known to combine the individual features of

carbon, B₄C and BN, and their properties are tunable depending on composition. As graphite-like materials are semimetallic, hexagonal boron nitride is insulating, therefore a hybrid B–C–N compound (between graphite and h-BN) can have outstanding semiconducting properties [8]. In particular cases, quasi-freestanding single-layer hexagonal boron nitride can be used as a substrate for graphene synthesis [9,10]. Several recent studies also indicated that h-BN atomic layers would be excellent dielectric layers to complement graphene electronics [11,12]. These layers could be sequentially grown on metal substrates to create the G/h-BN/metal stacked layers, which are certainly useful for various applications. This idea has led to a surge in investigations regarding the functionalization of h-BN [13–15].

Currently, the preparation and investigation of the graphene layer on non-metal substrates is one of the exciting areas in surface science [16, 17]. Moreover, the formation of graphene with the CVD method on a so-called “white graphene” surface (h-BN) is a great challenge, especially because the substrate boron nitride layer has “nanomesh” structure [5,6,18]. Furthermore, graphene growths on clean Rh(111) also

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results in a non-planar 2D carbon layer [19].

In our recent project, in addition to investigating the adsorption properties of cyclohexene and benzene on the h-BN/Rh(111) surface layer at cryogenic temperatures we also attempted to produce a graphene/h-BN sandwich system by the high temperature decomposition of the above mentioned C6 molecules. After the adsorption of benzene at 1000 K, we developed a graphene-like carbon structure on the surface of h-BN/Rh(111) without the removal or destruction of the h-BN film. The oxidation of the covering carbon layer led to CO production in agreement with the TPD measurements, and h-BN was completely recovered, which we confirmed by CO titration.

Our results were evidenced directly by Auger Electron Spectroscopy (AES) and indirectly by High Resolution Electron Energy Loss Spectroscopy (HREELS) and Mass Spectrometry (MS).

2. Experimental

The Rh(111) crystal used in this work was cut from a single crystal boule and was a product of Material Research Corporation (purity: 99.99%). It was mounted between two tantalum wires, which were connected via a copper block directly to a liquid nitrogen reservoir. Initially the sample was cleaned by repeated cycles of Ar⁺ sputtering (typically 1 kV, 1 × 10⁻⁷ mbar Ar, 300 K, 2 μA for 10–30 min) and annealing to 900–1100 K until no contaminations were detected by AES. The sample was heated resistively from 160 to 1100 K. Its temperature was monitored by a chromel-alumel thermocouple spot welded into the side of the crystal, and was controlled with a feedback circuit to provide a linear heating rate of ca. 10 K/s. Gases were dosed through a 0.1 mm diameter capillary that terminated at ~3 cm from the sample. The local pressure at the sample was about 10⁻⁷ mbar during dosing. The dosing temperature was ~160 K unless otherwise noted. The experimental work was performed in a two-level UHV chamber with a routine base pressure of 5 × 10⁻¹⁰ mbar produced by a turbomolecular pump. The chamber was equipped with facilities for AES, HREELS and TPD [20,21]. The HREEL spectrometer (LK, ELS 3000) was placed in the lower level of the chamber and had a resolution of 20–40 cm⁻¹ (FWHM). The count rates in the elastic peak were typically in the range of 1 × 10⁴ – 1 × 10⁵ counts-per-second (cps). All spectra reported were recorded with a primary beam energy of 6.5 eV and at an incident angle of 60° with respect

to the surface normal in the specular direction. Borazine of > 99.8% purity was the product of Katchem Ltd. Borazine was always stored at 254 K except when the doser was charged. All gas dosing lines were passivated and evacuated prior to borazine introduction.

3. Results and discussion

3.1. Characterization of the boron nitride layer

As we detailed in the Introduction, our main aim was to investigate the adsorption properties of different GR precursor molecules on the h-BN layer, as well as the possibilities of producing 2D sandwich structures containing a graphene layer on top of the BN nanomesh. To reach our goals we had to ascertain that the BN monolayer was continuous, and we did not have a large number of accessible free rhodium terraces on the surface. For this purpose, we examined the continuity of the h-BN layer on the Rh(111) single crystal with CO titration experiments. We exposed both the clean Rh(111) surface and the h-BN covered sample to 50 L of carbon monoxide. The HREELS results of the measurements are shown in Fig. 1.A.

CO adsorption with saturation coverage on clean Rh(111) resulted in the characteristic loss peaks of CO on the HREEL spectra (Fig. 1A. a.). We can identify the well-known characteristic modes of CO at 1860 and 2050 cm⁻¹ on the rhodium surface, where the lower and higher energy peaks are associated with the CO molecules adsorbed in the three-fold hollow site and the “atop” (onefold) site, respectively [22,23]. In a separate experiment (Fig. 1A. b.) we prepared the h-BN layer on clean Rh(111) to check the HREELS spectra of the nanomesh, as it was characterized in our former paper [18]. We could observe only the characteristic phonon peaks of the h-BN monolayer at 790 cm⁻¹, 1510 cm⁻¹ and with lower intensity as a shoulder at 1350 cm⁻¹. The first peak is the transversal optical (TO) phonon mode (out of plane polarization), the higher energy loss is the longitudinal optical (LO) phonon mode, while the shoulder at 1350 cm⁻¹ belongs to the transversal optical phonon with in-plane polarization. Our results are in good agreement with the literature data collected in Table 1.

In the next step, we added 50 L of CO to the h-BN nanomesh prepared on the Rh(111) single crystal at room temperature (Fig. 1A. c.). The CO losses present on the clean rhodium surface did not show up on the

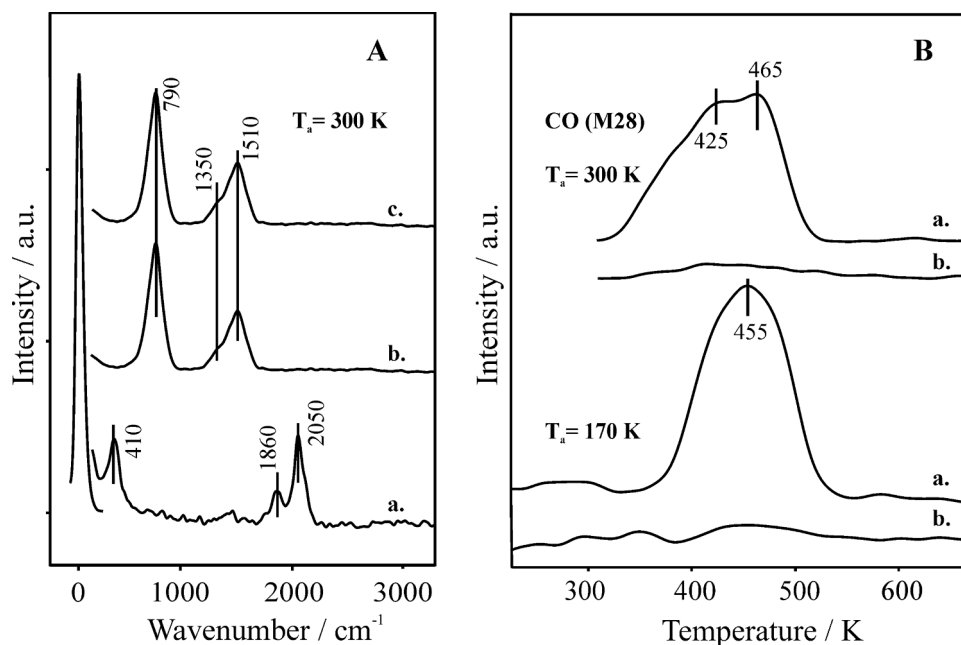


Fig. 1. HREEL spectra (A) from the CO covered Rh(111) (a.), the clean h-BN/Rh(111) (b.), and the CO saturated h-BN/Rh(111) (c.) surfaces at 300 K. CO exposure was 50 L in both cases. TPD curves for saturation CO M(28) coverages at 300 and 170 K (B) on clean Rh(111) crystals (a.) and on h-BN/Rh(111) surfaces (b.).

Table 1
The characteristic BN vibrations on certain surfaces [24].

System	TO _⊥ (cm ⁻¹)	TO _∥ (cm ⁻¹)	LO (cm ⁻¹)
h-BN/Ni(111)	728	1360	1360
h-BN/Pd(111)	784	1384	1432
h-BN/Pt(111)	792	1384	1464
h-BN/Rh(111) <i>this study</i>	790	1350	1510
Bulk h-BN	776, 824	1352, 1360	1600

boron nitride spectra. Hence, we can ascertain two statements: boron nitride has a low affinity to carbon monoxide adsorption at room temperature (RT) and CO does not bind to the surface of h-BN. Moreover, the relatively high dipole moment of CO (which should result in a loss peak even at low surface concentration) and the complete absence of CO peaks on the HREELS spectra taken from the BN covered rhodium sample assured us that we had successfully prepared a continuous h-BN nanomesh on the rhodium surface. It is generally known from literature that the formation of the second BN layer is not beneficial, and its development is energetically unfavorable [25]. Thus, we can say that we succeeded in creating a 2D monolayer h-BN film with only few defects in the structure. The produced layer could be a good template for further investigations without being directly affected by the rhodium adsorption sites.

We carried out temperature programmed desorption (TPD) measurements too in order to gather information about the stability of the h-BN monolayer and about the possible formation of adsorbed CO, which was not detected by HREELS. During our TPD measurements, carbon monoxide desorption was monitored at M(28) at 300 K and 170 K after adsorption (Fig. 1B.). In both experiments (at different temperatures) we marked with (a.) the desorption from the clean Rh(111) surface and with (b.) the h-BN/Rh(111) system, respectively. Due to its electron structure, the clean rhodium surface is capable, while boron nitride is not capable of CO adsorption. TPD measurements can also provide quantitative information on the continuity of the h-BN layer. CO desorption from Rh(111) surfaces occurred in the temperature range of 400–500 K. In contrast, we observed significant desorption of CO from the boron nitride surface neither at room nor at cryogenic (T_a=170 K) temperatures. This is consistent with the HREELS results and indicates the completed monolayer BN coverage. Nevertheless, when comparing the TPD peak areas in the two (clean and BN covered) cases we can conclude that at lower temperatures the highest M(28) CO peak area which we have ever observed on h-BN was ~9% compared to the clean Rh(111). This means that CO coverage is less than 0.054–0.068 ML on h-BN/Rh(111) [23]. Although this suggests that surface defects are certainly present on the h-BN/Rh(111) interface, their quantity is not likely to significantly affect our observations and the main directions of surface reactions.

3.2. Adsorption of C6 hydrocarbons on BN covered Rh(111) at low temperatures

3.2.1. Cyclohexene adsorption on h-BN/Rh(111)

Cyclohexene is commonly used as a probe molecule in catalytic reactions because its conversion is prototypical to other hydrocarbons on transition metal surfaces. Depending on the nature of the surface layer, this decomposition could produce surface carbon and desorbed hydrogen directly or through intermediates (e.g. benzene) [26,27]. There were also some cases in which complete desorption was observed without any sign of decomposition products [27]. Investigating cyclohexene and its derivative surface intermediates, like benzene as the smallest aromatic molecule, could be engaging also on 2D nanomesh, as it has the same hexagonal structure. Although the most commonly used materials in graphene production are C1–C3 hydrocarbons (e.g.: methane, ethene, ethane or propene), the behavior of the C6 molecules are interesting for the purpose of preparing graphene on non-metallic

h-BN, because their conjugated π-bonding structure is similar to that of graphene.

In this section, we would like to exhibit our results obtained from the h-BN covered Rh(111) surfaces following the adsorption of cyclohexene and benzene.

In this study we did not aim to investigate the adsorption properties of the above mentioned hydrocarbons on the clean Rh(111) surface, yet we collected the main HREEL spectroscopic and TPD data from the clean rhodium, too. The adsorption of 3 L cyclohexene on clean rhodium at 160 K produces vibration losses on the HREEL spectra at 645, 890, 1040, 1250, 1330, 1420, 2920 cm⁻¹, and a shoulder at 3020 cm⁻¹ (Fig. 2.a.). The latter peak belongs to the ν(C–H) vibration of olefinic bond in cyclohexene, which in this case is the sign of multilayer adsorption. The observed peaks are in good agreement with the condensed layer of cyclohexene [28]. The TPD results reinforced the HREELS observation, i. e. besides cyclohexene desorption at ~360 K only benzene and hydrogen desorbed from the surface at higher temperatures (not shown), and a significant part of benzene molecules completely dehydrogenated, producing surface carbon and hydrogen.

Adsorption of 3 L cyclohexene on the h-BN/Rh(111) surface resulted in a similar vibration spectrum as the clean surface, but it was supplemented with boron nitride phonon vibration peaks. However, the molecular peak positions and intensities showed a slight difference from those resulting from adsorption on the bare sample (Fig. 2.b-e.).

The two most conspicuous differences are the intensity decrease at 650 cm⁻¹ and the slightly increased shoulder appearance at 3020 cm⁻¹. The spectral changes and the drastic intensity loss above 160 K after adsorption suggest a very weak interaction between the boron nitride layer and the cyclohexene molecules. Above 300 K all the peaks connected to the C–H species disappeared from the spectra without any sign of dissociation, as it was concluded from the TPD results too (not shown).

As the only desorbing product after cyclohexene adsorption (on the clean metal surface) was benzene, it seemed logical to investigate its adsorption too.

3.2.2. Benzene adsorption on h-BN/Rh(111)

The adsorption of benzene on Rh(111) was investigated at room temperature in detail by G.A. Somorjai and coworkers where they have found that the saturation benzene coverage is 0.17 ML [29]. In our experiment low temperature (160 K) adsorption of 3 L benzene led to

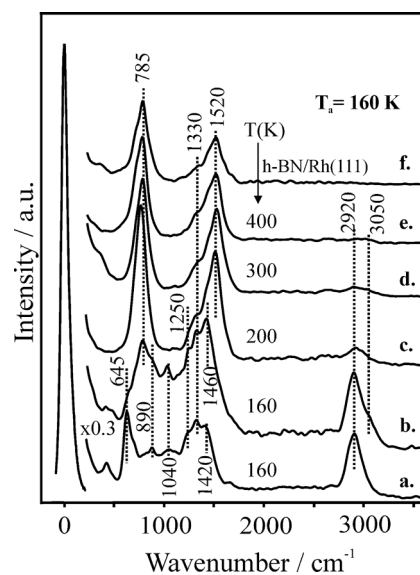


Fig. 2. Cyclohexene (3L) adsorption at 160 K on (a) clean Rh(111) (b) on h-BN/Rh(111) and (c-e) annealing of the surface layer; (f) clean h-BN/Rh(111) layer.

vibration losses at 680, 980, 1110, 1410, and 3060 cm^{-1} , which show good agreement with the observation on Pt(111) and Ni(111) surfaces after benzene multilayer adsorption (see Table 2). The appearance of these peaks strengthens our conclusions drawn during the decomposition measurements of cyclohexene on Rh(111) (Section 3.2.1.), i.e. that we had correctly identified the peaks according the dehydrogenation of olefin to benzene.

As it can be seen, the dominant peak is the vibration at 680 cm^{-1} in Fig. 3.A. This peak is related to an out-of-plane CH deformation vibration, which differs from the values of the gas phase spectra. The underlying reason can be found in the selection rules of HREELS. Following adsorption on metals, this change can occur if the molecules are adsorbed parallel to the surface, in other words, they lie on the surface. At the same time, there are still active in-plane modes on the spectra (980, 1113, 1410 cm^{-1}) with significantly lower intensities. There are only few possible explanations for this observation: 1.) The image charge (which is responsible for the selection rule) is absent, because the distance between the surface and the corresponding molecules in the multilayer is too large (8–10 Å). 2.) The CH bonds of the slightly perturbed benzene molecules can form an angle with the surface, as a result of which the losses – that can be assigned to these vibrations – appear in the spectrum. 3.) In some cases, one of the C–H bonds of the benzene molecules breaks and lets off a hydrogen atom and creates a σ -bond with a rhodium atom instead of the much weaker π -bond. Presumably, there are special adsorption centers on the sample surface (e.g., adatoms, edges) on which this form of bonding can also be beneficial. Yet, we can say that benzene primarily adsorbs parallel to the surface on the clean Rh(111).

At room temperature, a significant change occurred in the spectrum: the 680 cm^{-1} peak shifted towards 810 cm^{-1} . The position of this loss indicates that benzene molecules adsorbed on top position, just like on Pt(111) [30]. Further heating of the sample caused the complete desorption or decomposition of the adsorbed layer. Although we did not see significant sign of dissociation products on the HREEL spectra at specular directions, the intense 810 cm^{-1} loss peak at 600 K - due to an out-of-plane CH bending mode, $\gamma(\text{CH})$ - suggests that a part of benzene very likely decomposed to hydrocarbon fragments as it was observed in the literature [29].

In the next step, we investigated the adsorption of benzene on the h-BN/Rh(111) surface. Adsorption was carried out at a low temperature, and the effect of heating was also followed on the adsorption layer by the HREELS method. The lower spectrum shows the initial h-BN/Rh(111) layer followed by the adsorption of benzene at 160 K (Fig. 3.B.). It was found that the peak belonging to the first phonon mode of boron nitride broadened, and consequently a loss peak appeared at 710 cm^{-1} , besides the peaks at 1470 and around 3000 cm^{-1} . These observations are very similar to those made on the clean Rh(111) surface at multilayer benzene coverages (Fig. 3A), however the in-plane mode at 1110 cm^{-1} did not appear, and the intensity of the peak at around 3000 cm^{-1} was also very low. These findings are strong evidence of the surface parallel position of the molecules where benzene rings lie on the surface (according to the HREELS selection rule). Hence it is safe to say that at this coverage, benzene develops only a monolayer on the h-BN/Rh(111), primarily with parallel orientation. After heating the sample to higher temperatures, the loss peaks belonging to benzene disappeared from the spectra, and only the boron nitride phonon losses were observable at

250 K. Our attempt to find any other desorption product in addition to benzene in TPD was also unsuccessful (Fig. 3.C.). Although we can observe a slight contribution in the hydrogen desorption spectrum around 450 K, even if this is accepted as a hydrogen desorption peak, we can attribute it to the defect sites of the BN layer or the accessible rhodium atoms nearby. There is only a weak interaction between C_6H_6 and h-BN, and moreover, the latter proved to be completely inert to the split of benzene after low temperature exposures in this coverage regime.

3.3. High temperature stability and adsorption properties of the h-BN/Rh(111) surface towards C6 molecules

3.3.1. Cyclohexene adsorption on h-BN/Rh(111) at 1000 K

Although the h-BN/Rh(111) surface showed inertness to the conversion of hydrocarbons at and below room temperature, surface reactivity was tested at high temperature (~ 1000 K) in order to cover the 2D nanomesh layer by a carbon layer by decomposing C6 hydrocarbons. We exposed the surface to an increasing amount of cyclohexene at $T_a=1000$ K. This temperature is typically in the range where graphene production occurs on metal single crystal surfaces [31–33]. We followed the effects by surface analytical methods, i.e. using AES and HREELS (see Fig. 4.A. and B. below). After the first few experimental cycles (<6 L exposition), we did not observe any significant changes in AES. In the work of C. Oshima and coworkers, the heavy exposure of a pristine h-BN monolayer on Ni(111) to air or after covering the BN layer by monolayer graphene changed the spectrum drastically [34]. The soft phonon (90 meV; ~ 726 cm^{-1}) disappeared completely and only the normal one (100 meV; ~ 806 cm^{-1}) was observed after contaminating the system. In addition, the TO \parallel and LO phonons appeared separately on the spectra. Nevertheless, in contrast to their experience, in our case the exposure of cyclohexene at high temperatures only decreased the HREELS peak intensities, and no other change was observed. Accordingly, the AES peak to peak relative intensities of boron (B 175 eV) and nitrogen (N 385 eV) started to decrease, too (see Fig. 4.B.). Above 13 L, the intensities dropped back drastically, and at the same time, the AES carbon relative intensity started to increase significantly. After 37 L exposure, the BN phonon peak intensities were only one tenth of their original values, for which we had two possible explanations: we covered the 2D nanomesh by a carbon layer (graphene?) or we removed it in parallel with the build-up process of the carbon structure. To check this phenomenon, we oxidized the surface layer by a single 120 L oxygen treatment at 900 K, where oxidation parameters were set based on the publication by Steinrück et al. [35] considering the stability of the BN (which will be detailed in the next section). Then we made a surprising observation: we did not only remove the carbon layer (as confirmed by AES carbon peak diminution), but also made the BN phonon loss peaks disappear from the HREEL spectra. It is in contrast with the results observed on MG/h-BN/Ni(111), where the removal of the contaminants increased the intensity of the soft phonon peak and decreased the normal phonon peak [34]. It seemed that with the carburization process, we not only covered the BN layer but very likely we broke up the BN nanomesh and a carbon layer started to evolve in parallel with the decomposition of the insulating layer. Nevertheless, we can discover a certain regime between 20 and 30 L, where the two structures are both present on the surface, possibly as alternating BN and carbon islands.

Table 2
Characteristic vibrations of benzene on different surface layers below RT.

Vibration Modes	C_6H_6 on Pt(111)[30]	C_6H_6 on Rh(111) [this study]	C_6H_6 on h-BN/Rh(111) [this study]
$\nu(\text{metal-C})$	360		
$\omega(\text{C-H})$ out-of-plane	570,830	680	710
$\nu(\text{C-C})$	1420	1410	1470
$\omega(\text{C-H})$ in-plane	1130	1113	
$\nu(\text{C-H})$	3000	3060	3000

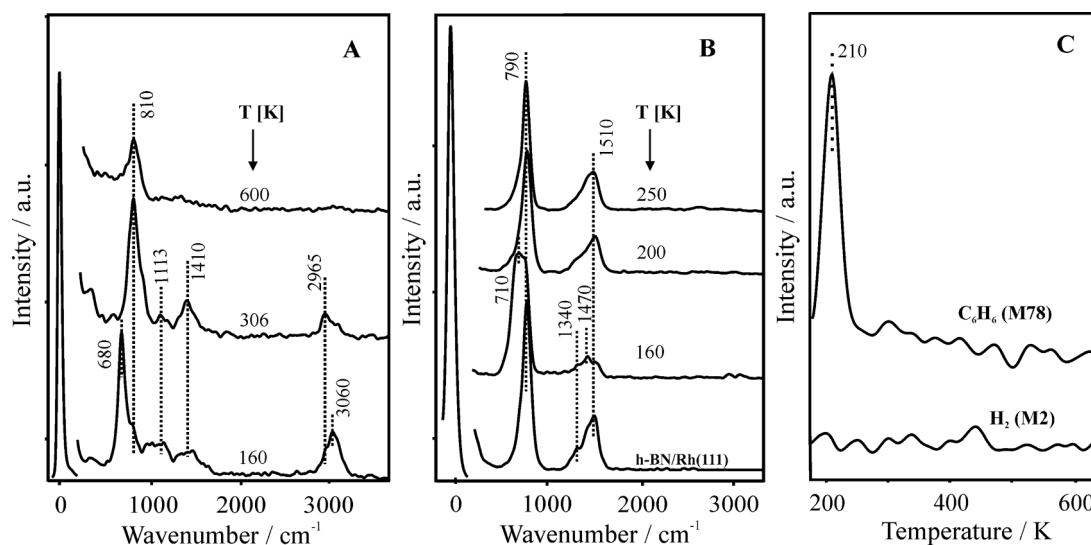


Fig. 3. Effects of annealing on the HREEL spectra after adsorption of 3 L benzene at 160 K on the clean Rh(111) single crystal (A) and on the h-BN/Rh(111) surface (B). TPD results collected after adsorption of 0.5 L benzene at 160 K (C).

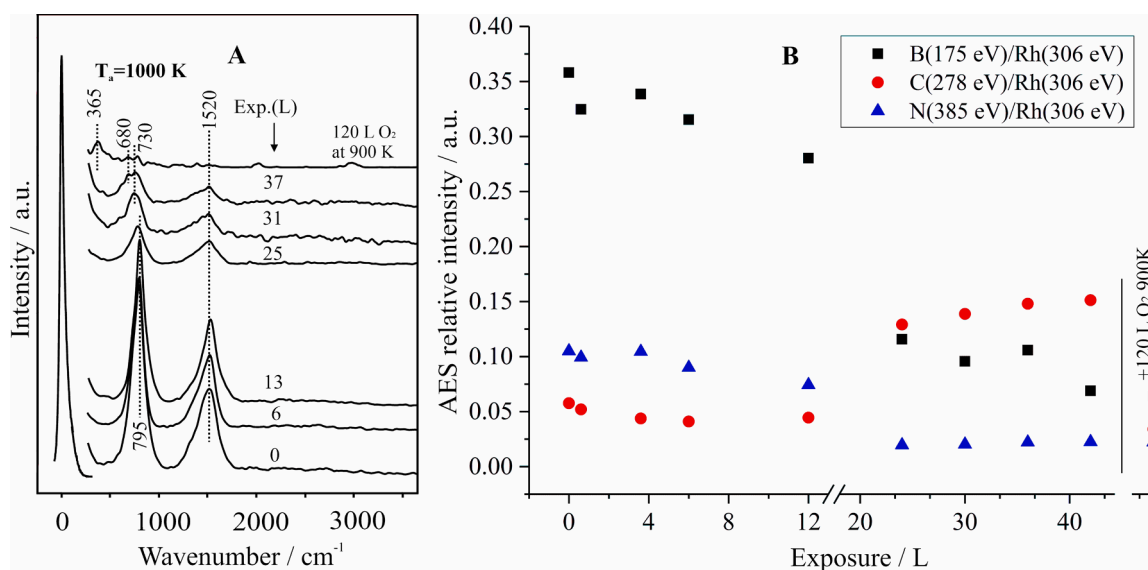


Fig. 4. Effect of exposure on HREEL spectra after cyclohexene adsorption on h-BN/Rh(111) surface at 1000 K and spectra recorded from the resulting layer after oxidation at 900 K (A); changes in relative intensities of AES peak ratios as a function of cyclohexene exposure ($T_a = 1000$ K) (B).

3.3.2. Stability of h-BN on Rh(111) against high temperature oxidation and hydrogen treatment

Hexagonal boron nitride nanomesh is known as a chemically inert and stable 2D monolayer on metal single crystal surfaces. This property makes it possible to easily grow a monolayer of BN, since even the building block molecules (e.g. borazine) do not decompose on its surface to produce the second layer. The production temperature is high (~1000–1100 K) therefore BN is not expected to decompose by itself, even in this temperature range. Nevertheless, we observed that after exposing the BN layer to cyclohexene at 1000 K, it broke up easily and following the oxidation process the remaining BN traces could be removed from the surface already at 900 K. In order to interpret the results, we consistently investigated the processes that may have taken place during the above experiment series, and which may have caused the decomposition of BN. One possible reason for this process may have been the high-temperature or/and oxygen treatment of the carbon covered layer. To prove or rule out this phenomenon, we treated the pure BN surface first in vacuum and then in oxygen at different

temperatures (900 and 1000 K) for 20 min (see Fig. 5.A).

It is interesting to mention that the oxygen functionalization of BN was recently achieved via a supersonic molecular beam [15]. However, in our case neither the vacuum annealing nor the 900 K oxygen treatment affected the boron peak intensity in AES. This also means that the applied oxidation treatment could not cause the BN layer to decompose parallel with the carbon layer. More likely, the BN layer had already broken up during the high-temperature (1000 K) treatment by cyclohexene and then reacted with the dissociation products of hydrocarbons. Hydrogen experiments were also performed to test this explanation, as cyclohexene produces a significant amount of hydrogen during its decomposition. In Fig. 5.B we demonstrate the results of this experiment. As we can see, after exposing the surface to 1260 L of hydrogen at 1000 K, BN started to break up as evidenced by the appearance CO-Rh HREELS losses at around 1900–2000 cm^{-1} . (CO originated from background adsorption during HREELS measurements at 300 K.) After further exposure at high temperatures, the BN phonon peaks disappeared, and the CO peaks dominated the spectrum. These findings

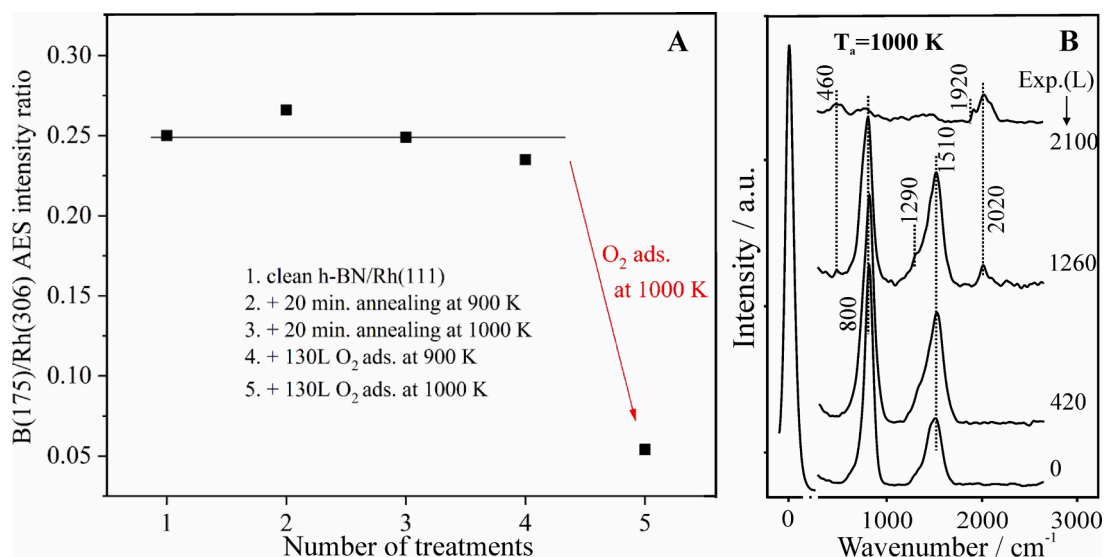


Fig. 5. Changes in the AES intensity ratio – B(175)/Rh(306) – after the oxidation of the sample at 900 and 1000 K (A) and HREEL spectra obtained after the adsorption of an increasing amount of hydrogen at 1000 K on the clean h-BN surface (B).

strengthen the former idea according to which during high temperature cyclohexene treatment the BN structure collapsed, probably due to the generated hydrogen. This led to the build-up of a carbon layer in the place of BN on the Rh(111). It was recently found that treatment with atomic hydrogen caused a defined modification in the pores of h-BN [15].

3.3.3. Benzene adsorption on h-BN/Rh(111) at 1000 K

In the light of the above observations and due to the much lower hydrogen content (and higher C/H ratio) of benzene it became even more interesting to study the high-temperature decomposition of benzene. Furthermore, it was also used as a precursor in graphene production on single crystal surfaces [31]. In the case of benzene, we expected that during the high temperature adsorption treatment BN would either not decompose, or would do so at a smaller rate. A possible consequence may be the formation of a carbon/graphene layer on its surface, and consequently the formation of a sandwich structure of graphene/h-BN/Rh.

The high temperature (1000 K) adsorption of benzene was followed

by steeply increasing exposure cycles in the following series of measurements (Fig. 6.A).

It is clearly observable that after the initial spectrum, in which only the loss peaks of the h-BN phonon could be seen, no new HREEL peaks appeared even after highly increased benzene exposures. This is in line with our expectations, i.e. no molecular adsorption is expected at this temperature, and at the same time, no surface carbon structure providing a loss spectrum can form in the studied wavelength range. Nevertheless, a significant decrease occurred after four cycles of treatment. We can link two explanations to our observations in this case. We covered the BN layer with a carbon structure as a result of the high temperature decomposition of benzene. The BN phonon peaks lose intensity because of the shielding effect of the dynamical dipole fields induced by free carriers in the carbon (graphene?) over-layer. Another possibility is that we broke BN down – similarly to the cyclohexene measurements – because of the high temperature treatment. However, while the intensity decreased, the existing peaks did not shift, and no new peaks appeared.

In our former study [7] HREELS spectra of the nanomesh itself

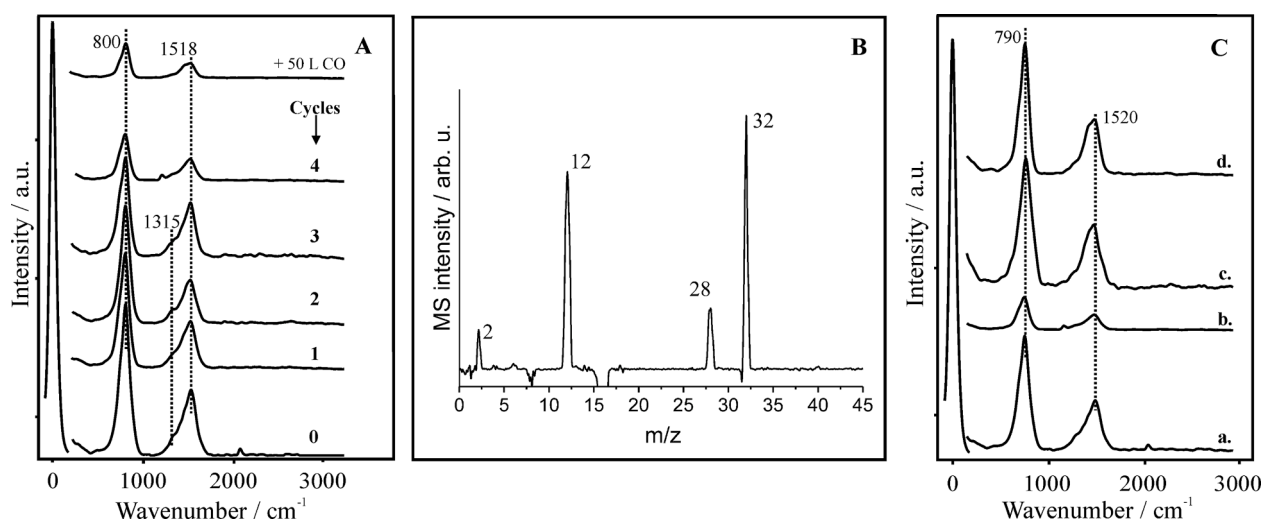


Fig. 6. Effects of exposure on the HREEL spectra after benzene adsorption on h-BN/Rh(111) at 1000 K. One cycle means $\sim 1100 \text{ L}$ exposure (A). Mass spectra taken during the oxidation of the sample at 900 K (subtracted spectra). (B). HREEL spectra from the clean h-BN/Rh(111) surface (a.), after benzene adsorption at 1000 K (4th cycle, $\sim 4400 \text{ L}$) (b.), after the oxidation of the b. layer (c.) and after the saturation of the oxidized layer with CO (d.) (C).

obtained at different angles of incidence and a steep intensity loss is observed for the out-of-plane TO_⊥ mode (785 cm⁻¹) at the off-specular geometries and a much milder angular dependence was found for the in-plane LO mode (1510 cm⁻¹). In this study, we not only varied the scattering geometry (specular, 10 and 20 off-specular), but we also carried out some measurements at different primary energies (6.5 and 10 eV) in particular to tune the information depth and obtain new structures e.g. the phonon features typical for graphene and/or graphite [36,37]. The BN phonon peak intensities decreased as well but we did not obtain any new features on the HREEL spectra. It should be mentioned that the positions of graphene sheet phonons (peak max. at 105 and 198 meV) and the BN phonons are very close to each other and can be overlapped.

In order to analyze the continuity of the topmost layer, carbon monoxide was first adsorbed onto the surface with high exposure (for 5 min at 6.7 × 10⁻⁷ mbar) at 300 K (the applied exposure was more than what we needed to saturate the clean Rh(111) surface). The result shows the absence of CO-Rh loss peaks, which suggests the lack of available rhodium atoms on the surface for CO molecules. For the further characterization of the produced heterostructure, the sample was oxidized at 900 K and gaseous products in the vacuum chamber were analyzed by mass spectrometry (see Fig. 6.B). In the corresponding figure we can see the subtracted spectrum of the two background MS measurements taken at room temperature and at 900 K. There is a significant difference between high- and low-temperature oxidation, which is also evidenced by the fact that sample treatment at 900 K produced peaks at mass numbers 16 and 28. This refers to the presence of CO formation in the gas phase. These contributions prove that carbon was oxidized off the sample surface, and as a consequence, the carbon layer was successfully removed from the h-BN/Rh(111) by oxygen treatment. HREELS measurements – performed in parallel with MS measurements – were consistent with this assumption, i.e. the phonon peaks of BN were re-amplified and strengthened in intensity without an observable shift (Fig. 6.C). The continuity of the recovered BN layer was confirmed again by CO adsorption experiments, where the absence of CO peaks indicated the integrity of the nanomesh layer and the absence of available rhodium centers. In this experiment we successfully created a contiguous carbon structure without the destruction or damage of the h-BN film.

3.3.4. Identification of the composed sandwich structures by Auger spectroscopy

In our study, exploring the nature of the produced carbon layer(s) was the next thing we examined. In order to obtain information on the chemical state of the carbon layer we not only produced different types of carbon structures by varying the decomposition temperature of C₆ hydrocarbons, but we also compared their spectra to the carbon Auger features, which appeared after exposing clean Rh(111) to ethene at

1000 K (Fig. 7.). In Fig. 7A, starting from 800 K we increased not only the production temperatures but also the exposure of cyclohexene. The position of the carbon peak shifted gradually from 276 eV until it approached the value characteristic of graphene produced by the recipe using ethylene at 1000 K [31,32]. At the same time, the B(KVV) peak at 175 eV decreased drastically in intensity with the increasing exposure of cyclohexene (Fig. 7b-d.). This suggested that the boron nitride layer was not only covered by the carbon layer, but it also decomposed. Based on these observations and in the light of the above mentioned HREELS and TPD results we can say that a graphene-like carbon layer was produced in parallel with the BN nanomesh decomposition. This process resulted possibly in an alternating BN/GR like carbon monolayer on the Rh(111) surface.

The results of the Auger electron spectroscopy (AES) measurements after benzene decomposition can be followed in Fig. 7B. Using AES peak positions and shapes we can distinguish the forms of the carbon layer, i.e. graphite, carbide and graphene, which give a slightly different Auger spectrum. We compared the Auger peaks of the clean h-BN/Rh(111) surface (a) to our carbon covered h-BN structure (b) and finally we also demonstrated the AES spectrum taken after ethene adsorption at 1000 K on the clean Rh(111). This latter spectrum – based on literature data [32] – represents the characteristic carbon peak position and shape of the graphene layer (c). We can conclude that the carbon (KLL) peak at a kinetic energy of 279 eV could be assigned to a graphene-like structure in both b and c cases. At the same time, the B(KVV) peak on spectrum b did not decrease to such an extent as it was observable in case of cyclohexene adsorption. This also strengthens the results of our HREELS measurements, i.e. that the observed carbon layer formed without the decomposition of the BN nanomesh. Although the catalytic center involved in the decomposition of C₆ hydrocarbons cannot be unambiguously identified by our measurement methods, we suppose that boron and rhodium atoms – at the BN nanomesh defect sites – initiate dissociation processes and carbon layer growth. Similar processes took place during our former experiments with ethanol conversion on Au/h-BN/Rh(111) surface, where boron atoms, especially those neighboring the gold nanoparticles at the pore region, played a significant role in the dehydrogenation of ethanol [21]. Based on these results we can conclude that we created a graphene like carbon structure on top of h-BN/Rh(111) nanomesh surface through the high temperature decomposition of benzene.

4. Conclusions

In this study we investigated the adsorption of C₆ hydrocarbons – cyclohexene and benzene – on h-BN covered Rh(111) surfaces both at low and at high temperatures. There is only a weak interaction between C₆H₆ and h-BN, therefore hexagonal boron nitride proved to be completely inert to the split of benzene after low temperature exposures.

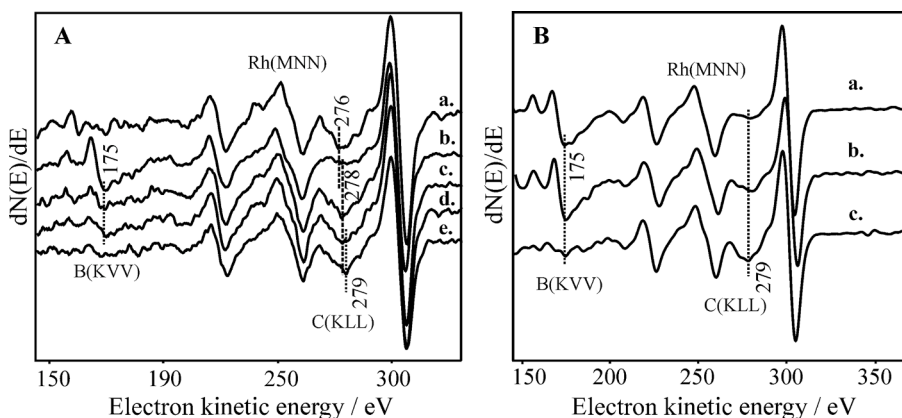


Fig. 7. Auger spectra of samples (A) after adsorption of (a) 3 L C₆H₁₀ on Rh(111) at 800 K, (b) 12 L C₆H₁₀ on h-BN/Rh(111) at 1000 K, (c) 24 L C₆H₁₀ on h-BN/Rh(111) at 1000 K, (d) 30 L C₆H₁₀ h-BN/Rh(111) at 1000 K and (e) graphene on Rh(111) produced by 90 L C₂H₄ adsorption on clean Rh(111) at 1000 K. (B) Auger spectra from the (a) initial clean h-BN/Rh(111) surface, (b) after 2300 L of C₆H₆ adsorption on h-BN/Rh(111) at 1000 K and (c) graphene on Rh(111) produced by 90 L of C₂H₄ adsorption on clean Rh(111) at 1000 K (B). The Auger transitions of Rh(MNN) at 222, 256 and 302 eV are not labeled on the Figures.

Nevertheless, these results gave some information about the monolayer coverage and parallel adsorption orientation of benzene on the 2D layer. Hexagonal boron nitride nanomesh is known as a chemically inert and stable 2D monolayer above metal single crystal surfaces. Using CO titration, we tested our h-BN preparation method and the produced monolayer. The measurements suggested that surface defects were certainly present on the h-BN/Rh(111) interface, but their quantity was under our detection limit. We also tested the layer via high temperature oxygen and hydrogen treatment. In both cases, after extremely high exposures of these molecules, the BN layer collapsed and decomposed at 1000 K. Although the h-BN/Rh(111) surface showed inertness to the conversion of hydrocarbons at and below room temperature, surface reactivity was tested at high temperature (~1000 K) in order to decompose C6 hydrocarbons to cover the 2D nanomesh by a carbon layer, hopefully by graphene. It seemed that with the HT decomposition of cyclohexene we not only covered the BN but we also broke up the nanomesh, and the carbon layer started to evolve in parallel with the decomposition of the insulating layer. However, we were able to define a certain exposure where both structures appeared on the surface, possibly as alternating BN and graphene layers. In contrast, after the high temperature (1000 K) adsorption of benzene we successfully created a contiguous – graphene-like – carbon structure without destroying or damaging the h-BN nanomesh produced on the Rh(111) surface.

CRedit authorship contribution statement

Ádám Sztítás: Visualization, Investigation, Writing – original draft. **Arnold P. Farkas:** Conceptualization, Supervision, Writing – original draft, Writing – review & editing. **Viktória Faur:** Visualization, Investigation. **Nikolett Bera:** Visualization, Investigation. **János Kiss:** Writing – review & editing. **Zoltán Kónya:** Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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