

Adsorption and reaction of SO₂ on graphene/ruthenium(0001) - an ultra-high vacuum surface science study

Thomas Stach, Melody C. Johnson, Samuel Stevens, Uwe Burghaus
Department of Chemistry and Biochemistry, NDSU, Fargo, ND

uwe.burghaus@ndsu.edu

Research presented was supported by ND EPSCoR
ND EPSCoR STEM Solicitation – Seed Award

Uwe Burghaus

**- Surface Chemistry | Het. Catalysis | Nanoscience | Materials -
North Dakota State University, Dept. Chemistry & Biochemistry**

uwe.burghaus@ndsu.edu

www.uweburghaus.us

<https://www.ndsu.edu/chemistry/people/faculty/burghaus.html>

Motivation – why study surface chemistry of sulfur compounds?

North Dakota State University

Basic science interest

- SO₂, is known for its rich and fairly complicated surface chemistry
- sulfur compounds appear quite reactive on graphene (liquid phase, powder samples, theory) **but** Not much surface science information for SO₂, H₂S on graphene
- use in noble metal-free catalysis

Applications

- acid rain (sulfuric acid) formation
- air pollution (volcanic activity, exhaust gas in power plants/transportation)
- corrosion of metals
- catalyst poisoning by sulfur

uwe.burghaus@ndsu.edu

Uwe Burghaus

**- Surface Chemistry | Het. Catalysis | Nanoscience |
Materials -**

**North Dakota State University, Dept. Chemistry &
Biochemistry**

uwe.burghaus@ndsu.edu

www.uweburghaus.us

**https://www.ndsu.edu/chemistry/people/faculty/burghaus.
html**

**Is there any evidence that graphene and functionalized
graphene can act as a catalyst?**

Given the literature there is no doubt that noble metal free catalysis does work. Examples of noble metal free carbon

catalysts are outlined in many published works (see, e.g., refs.¹⁻²¹). Many studies concern synthetic organic chemistry in the liquid phase.²² For example, phenol oxidation by graphene oxide was reported in the liquid phase.¹⁷ Or, the Friedel–Crafts reaction of benzene using mesoporous carbon nitrides is described.¹⁸ Or, graphene oxide was used to catalyze the oxidation of alcohols in the liquid phase.¹⁹ (See e.g. Tabs. 1-2 in ref.²³ for further examples and references.) Importantly, adsorption and reaction processes of sulfur compounds with GO have been studied extensively in the liquid phase^{11, 13, 14, 24-27} as well as theoretically.²⁵

Photocatalytic processes in the gas-phase on graphitic system were reported too such as CO₂ to methanol conversion,²⁸ just to mention one study here. For noble metal free electrocatalysis see e.g. ref.²⁹

Ambient pressure gas phase reactions are also known. For example, mesoporous carbon acts as a metal-free catalyst for the low-temperature H₂S oxidation by doping the carbon catalyst with nitrogen atoms.¹⁶ Ref.³⁰ describes a high pressure study on an apparently thick layer of supported commercial GO flakes. On that system, CO oxidation (as a gas-surface reaction) was seen successfully at high pressure conditions.³⁰ On N and S doped graphene flakes NO dissociation was seen using a fixed-bed reactor.²⁰

In addition, many theoretical studies suggest that graphene and graphene oxide can work as a catalyst. For example, SO₂ oxidation by graphene oxide was considered by

density functional theory (DFT).²⁵ In another DFT study an enhancement of NO_x and N₂O₂ adsorption on hydroxyl and carbonyl covered GO, compared with graphene, was theoretically predicted. Here hydrogen bond formation and even weak covalent bonds (by hybridization of NO_x and GO bonds) were invoked.³¹ Similar theoretical results were reported about ammonia (NH₃) adsorption on GO.³²

Non carbon but noble metal free catalysts are also known.³³

Molecular adsorption was studied also experimentally on (functionalized) graphene³⁴⁻⁴³ but, experimental UHV surface science work characterizing surface reactions has apparently not been conducted, except our own works.⁴⁴

A concern often voiced is whether graphene can really act as a catalyst in these processes. In some of the literature examples just discussed, the reactions may be stoichiometric, but also examples are known where graphene clearly acts as a catalyst. Citing directly the review about graphene in organic liquid phase reactions:²² "... GO was recovered and reused for nine catalytic cycles..." (see page 11474, right column, ref.²²) That exactly is the definition of a catalyst. That citation concerns Michael addition reactions, similar results were obtained for C–H bond activation of aryl halides (see page 11475, left column in the same review). For other examples, see e.g. refs.⁴⁵ (defects in graphene acting as active sites), ref.^{34, 35} (enhanced CO adsorption, graphene was not altered, i.e., the process is catalytic), ref.¹⁵ (Si doped graphene catalyzing

CO oxidation), etc.

References

- 1 Su, D. S., Zhang, J., Frank, B., Thomas, A., Wang, X., Paraknowitsch, J. Schloegel, R., "Metal-Free Heterogeneous Catalysis for Sustainable Chemistry (review)" *ChemSusChem* **3**, 169–180, (2010).
- 2 Schreiner, P. R., "Metal-free organocatalysis through explicit hydrogen bonding interactions" *Chem. Soc. Rev.* **32**, 289–296., (2003).
- 3 Zhang, J., Su, D., Zhang, A., Wang, D., Schloegel, R. Hbert, C., "Nanocarbon as Robust Catalyst: Mechanistic Insight into Carbon-Mediated Catalysis" *Angew. Chem. Int. Ed.* **46**, 7319 –7323, (2007).
- 4 Wang, Y., Li, H., Yao, J., Wang, X. Antonietta, M., "Synthesis of boron doped polymeric carbon nitride solids and their use as metal-free catalysts for aliphatic C–H bond oxidation" *Chem. Sci.* **2**, 446–450, (2011).
- 5 Xiaoyan, S., Rui, W. Dangsheng, S., "Research progress in metal-free carbon-based catalysts" *Chinese Journal of Catalysis* **34**, 508–523, (2013).
- 6 Qi, W. Su, D., "Metal-Free Carbon Catalysts for Oxidative Dehydrogenation Reactions" *ACS Catal.* **4**, 3212–3218, (2014).
- 7 Sun, H., Wang, Y., Liu, S., Ge, L., Wang, L., Zhub, Z. Wang, S., "Facile synthesis of nitrogen doped reduced graphene oxide as a superior metal-free catalyst for

- oxidation" *Chem. Commun.* **49**, 9914-9916, (2013).
- 8 Sakaushi, K., Fellingner, T. P. Antonietti, M., "Bifunctional Metal-Free Catalysis of Mesoporous Noble Carbons for Oxygen Reduction and Evolution Reactions" *ChemSusChem* **8**, 1156 – 1160, (2015).
- 9 Zhang, M. Dain, L., "Carbon nanomaterials as metal-free catalysts in next generation fuel cells" *Nano Energy* **1**, 514–517, (2012).
- 10 Dai, L., Xue, Y., Qu, L., Choi, H. Baek, J., "Metal-Free Catalysts for Oxygen Reduction Reaction" *Chem. Rev.* **115**, 4823–4892, (2015).
- 11 Zhai, C., Sun, M., Zhua, M., Song, S. Jiang, S., "A new method to synthesize sulfur-doped graphene as effectivemetal-free electrocatalyst for oxygen reduction reaction" *Applied Surface Science* **407**, 503–508, (2017).
- 12 Tang, Y., Chen, W., Shen, Z., Chang, S., Zhao, M. Dai, X., "Nitrogen coordinated silicon-doped graphene as a potential alternative metal-free catalyst for CO oxidation" *Carbon* **111**, 448-458, (2017).
- 13 Zhao, Q., Mao, Q., Zhou, Y., Wei, J., Liu, X., Yang, J., Luo, L., Zhang, J., Chen, H., Chen, H. Tang, L., "Review: Metal-free carbon materials-catalyzed sulfate radical-based advanced oxidation processes: A review on heterogeneous catalysts and applications" *Chemosphere* **189**, 224-238, (2017).
- 14 Esrafil, M. D., Saeidi, N. Nematollahi, P., "Si-doped graphene: A promising metal-free catalystfor oxidation of SO₂" *Chemical Physics Letters* **649**, 37–43, (2016).
- 15 Tang, Y., Liu, Z., Dai, X., Yang, Z., Chen, W., Ma, D. Lu,

- Z., "Theoretical study on the Si-doped graphene as an efficient metal-free catalyst for CO oxidation" *Applied Surface Science* **308**, 402–407, (2014).
- 16 Sun, F., Liu, J., Chen, H., Zhang, Z., Qiao, W., Long, D. Ling, L., "Nitrogen-Rich Mesoporous Carbons: Highly Efficient, Regenerable Metal-Free Catalysts for Low-Temperature Oxidation of H₂S" *ACS Catal.* **3**, 862–870, (2013).
- 17 Komeily-Nia, Z., Chen, J. Y., Nasri-Nasrabadi, B., Lei, W. W., Yuan, B., Zhang, J., Qu, L. T., Gupta, A. Li, J. L., "The key structural features governing the free radicals and catalytic activity of graphite/graphene oxide" *Phys.Chem.Chem.Phys.* **22**, 3112, (2020).
- 18 Goettmann, F., Fischer, A., Antonietti, M. Thomas, A., "Chemical Synthesis of Mesoporous Carbon Nitrides Using Hard Templates and Their Use as a Metal-Free Catalyst for Friedel–Crafts Reaction of Benzene" *Angew. Chem. Int. Ed.* **45**, 4467–4471, (2006).
- 19 Dreyer, D. R., Jia, H. P. Bielawski, C. W., "Graphene Oxide: A Convenient Carbocatalyst for Facilitating Oxidation and Hydration Reactions" *Angew. Chem.* **122**, 6965 –6968, (2010).
- 20 Wang, Y., Shen, Y., Zhou, Y., Xue, Z., Xi, Z. Zhu, S., "Heteroatom-Doped Graphene for Efficient NO Decomposition by Metal-Free Catalysis" *ACS Appl. Mater. Interfaces* **10**, 36202–36210, (2018).
- 21 Wu, S., Yu, L., Wen, G., Xie, Z. Lin, Y., "Recent progress of carbon-based metal-free materials in thermal-driven catalysis" *Journal of Energy Chemistry* **58**, 318–335, (2021).

- 22 Mohammadi, O., Golestanzadeh, M. Abdouss, M., "Recent advances in organic reactions catalyzed by graphene oxide and sulfonated graphene as heterogeneous nanocatalysts: a review" *New J. Chem.* **41**, 11471--11497, (2017).
- 23 Su, C. Loh, K. P., "Carbocatalysts: Graphene Oxide and Its Derivatives" *Acc. Chem. Res.* **46**, 2275–2285, (2013).
- 24 Long, Y., Zhang, C., Wang, X., Gao, J., Wang, W. Liu, Y., "Oxidation of SO₂ to SO₃ catalyzed by graphene oxide foams" *J. Mater. Chem.* **21**, 13934, (2011).
- 25 He, G. He, H., "DFT studies on the heterogeneous oxidation of SO₂ by oxygen functional groups on graphene" *Phys. Chem. Chem. Phys.* **18**, 31691--31697 (2016).
- 26 Gotterbarm, K., Spath, F., Bauer, U., Steinruck, H. P. Papp, C., "Adsorption and Reaction of SO₂ on Graphene-Supported Pt Nanoclusters" *Top Catal* **58**, 573–579, (2015).
- 27 Rad, A. S. Zareyee, D., "Adsorption properties of SO₂ and O₃ molecules on Pt-decorated graphene: A theoretical study" *Vacuum* **130**, 113-118, (2016).
- 28 Hsu, H.-C., Shown, I., Wei, H.-Y., Chang, Y.-C., Du, H.-Y., Lin, Y.-G., Tseng, C.-A., Wang, C.-H., Chen, L.-C., Lind, Y.-C. Chen, K.-H., "Graphene oxide as a promising photocatalyst for CO₂ to methanol conversion" *Nanoscale* **5**, 262, (2013).
- 29 Wang, J., Wang, P., Wang, S. Li, J., "A metal-free catalyst: sulfur-doped and sulfur nanoparticle-modified CMK-3 as an electrocatalyst for enhanced N₂-fixation" *New J. Chem.* **44**, 20935, (2020).
- 30 Narayanan, B., Weeksa, S. L., Jariwala, B. N., Macco, B., Weber, J. W., Rathi, S. J., Sanden, M. C. M., Sutter, P.,

Agarwal, S. Ciobanu, C. V., "Carbon monoxide-induced reduction and healing of graphene oxide" *Journal of Vacuum Science & Technology* **A31**, 040601 (2013).

31 Tang, S. Cao, Z., "Adsorption of nitrogen oxides on graphene and graphene oxides: Insights from density functional calculations" *THE JOURNAL OF CHEMICAL PHYSICS* **134**, 044710, (2011).

32 Tang, S. Cao, Z., "Adsorption and Dissociation of Ammonia on Graphene Oxides: A First-Principles Study" *J. Phys. Chem. C* **116**, 8778–8791, (2012).

33 Royer, S., Duprez, D., Can, F., Courtois, X., Batiot-Dupeyrat, C., Laassiri, S. Alamdari, H., "Perovskites as Substitutes of Noble Metals for Heterogeneous Catalysis: Dream or Reality" *Chem. Rev.* **114**, 10292–10368, (2014).

34 Elias, D. C., Nair, R. R., Mohiuddin, T. Morozov, S. V., "Control of graphene's properties by reversible hydrogenation: evidence for graphane" *Science* **323**, 610-613, (2009).

35 Balog, R., Jørgensen, B., Wells, J., Lægsgaard, E., Hofmann, P., Besenbacher, F. Hornekær, L., "Atomic Hydrogen Adsorbate Structures on Graphene" *J. AM. CHEM. SOC.* **131**, 8744–8745, (2009).

36 Sivapragasam, N., Nayakasinghe, M. T. Burghaus, U., "Adsorption Kinetics and Dynamics of CO₂ on Ru(0001) Supported Graphene Oxide" *Journal of Physical Chemistry C* **120**, 28049–28056, (2016).

37 Chakradhar, A., Sivapragasam, N., Nayakasinghe, M. T. Burghaus, U., "Adsorption Kinetics of Benzene on Graphene: an Ultra-high Vacuum Study" *Journal of Vacuum*

Science & Technology A **34**, 021402, (2016).

38 Sivapragasam, N., Nayakasinghe, M. T. Burghaus, U., "Adsorption of n-butane on graphene/Ru(0001)—A molecular beam scattering study" J. Vac. Sci. Technol. **34**, 041404, (2016).

39 Chakradhar, A. Burghaus, U., "Adsorption of water on graphene/Ru(0001)—an experimental ultra-high vacuum study" Chemical Communications **50**, 7698 - 7701, (2014).

40 Burghaus, U., "Adsorption of water on two-dimensional crystals: water/graphene and water/silicatene (short review)" Inorganics **4**, 10; <http://www.mdpi.com/2304-6740/4/2/10/pdf> (2016).

41 Chakradhar, A., Trettel, K. M. Burghaus, U., "Benzene adsorption on Ru(0001) and graphene/Ru(0001) — How to synthesize epitaxial graphene without STM or LEED?" Chemical Physics Letters **590**, 146-152, (2013).

42 Sivapragasam, N., Nayakasinghe, M. T., Chakradhar, A. Burghaus, U., "Effects of the support on the desorption kinetics of n-pentane from graphene: an ultra-high vacuum adsorption study" J. Vac. Sci. Technol. A **35**, 061404, (2017).

43 Chakradhar, A., Sivapragasam, N., Nayakasinghe, M. T. Burghaus, U., "Support effects in the adsorption of water on CVD graphene: an ultra-high vacuum adsorption study," Chemical Communications **51**, 11463 - 11466, (2015).

44 Stach, T., Johnson, M. C., Stevens, S. Burghaus, U., "Adsorption Kinetics of SO₂ on Graphene: an Ultra-high Vacuum Surface Science Study" submitted (2021).

45 Widjaja, H., Oluwoye, I., Altarawneh, M., Hamra, A. A. B., Lim, H. N., Huang, N. M., Yin, C. Y. Jiang, Z. T., "Phenol

dissociation on pristine and defective graphene" Surface Science **657**, 10-14, (2017).

Literature SO₂

North Dakota State University

decomposes on all metal surfaces,
except silver.

The more reactive the surface, the lower the
onset temperature of dissociation.

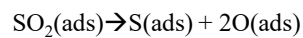
SO₂/ HOPG → molecular adsorption
polar / non-polar

but

S, S_x, SO, SO₃, SO₄, S—O complex

- support effects
- polarization effects
- modification of density of states
- hybridization
- reactive defects in graphene

Ru surfaces are very reactive towards SO₂
decomposition even at low temperatures

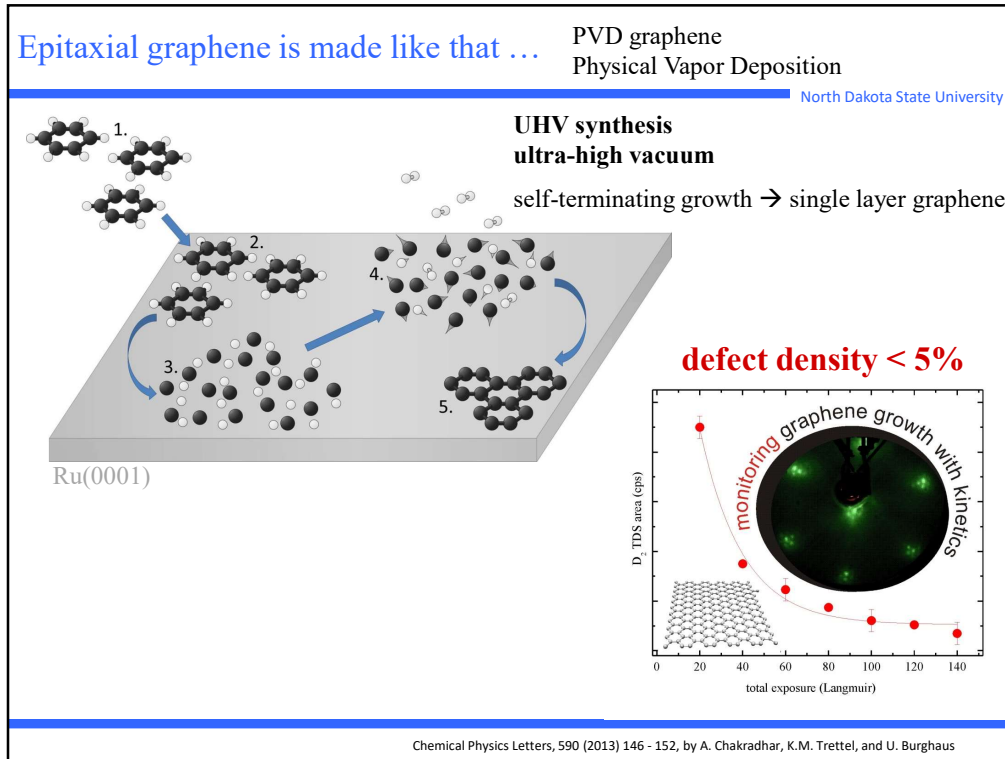


on Ru desorption of sulfur already at 250 K

uwe.burghaus@ndsu.edu

HOPG - highly oriented pyrolytic graphite

Graphitic surfaces. Following simple chemistry concepts, polar SO₂ is predicted to interact only weakly with graphene since carbon surfaces are considered as non-polar. However, substrate effects are known in the literature to be caused by polarization effects where some of the van der Waals interactions of the substrate are transmitted through the graphene layer. Also, modification of the density of states at the Fermi level induced by the graphene–substrate interaction are known to occur.

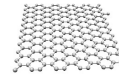


Graphene was made by decomposing benzene on ruthenium, see

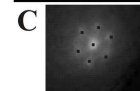
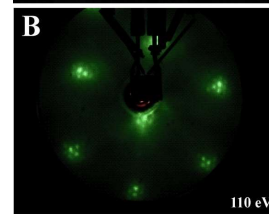
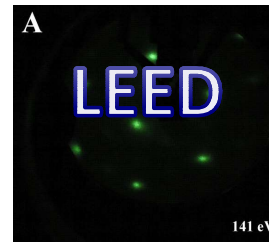
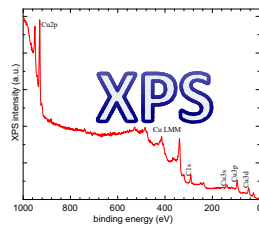
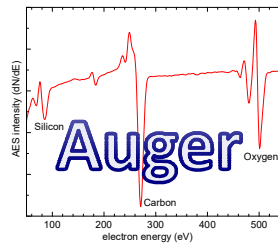
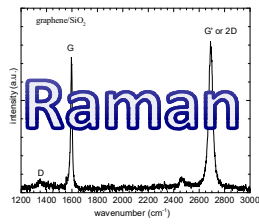
Benzene adsorption on Ru(0001) and graphene/Ru(0001) — How to synthesize epitaxial graphene without STM or LEED?

Chemical Physics Letters, 590 (2013) 146 - 152,
by A. Chakradhar, K.M. Trettel,* and U. Burghaus
*NSF REU fellow

You would not like to see this ... sample characterization

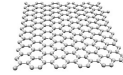


North Dakota State University

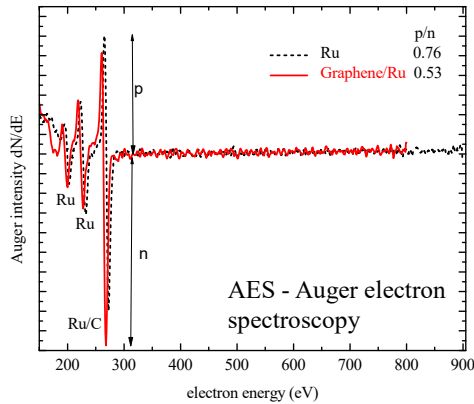


XPS: X-ray Photoelectron Spectroscopy
LEED: Low Energy Electron Diffraction

Auger - sample characterization



North Dakota State University



AES peak position for $E_p = 3\text{keV}$	
C	272
Ru	273, 231, 200, 184, 176, 150, 37
S	152
O	503, 483, 468

Ru(0001)	Graphene/Ru(0001)	Ref.
---	0.5	Z. Zhou, B.F. Habenicht, Q. Guo, Z. Yan, Y. Xu, L. Liu, D.W. Goodman, Surf. Sci. 611 (2013) 67
0.8	0.46	Li Liu a, Zihao Zhou a, Qinlin Guo b, Zhen Yan a, Yunxi Yao a, D. Wayne Goodman, Surface Science 605 (2011) L47–L50
0.76 ± 0.02	0.34 ± 0.02	A. Chakradhar, K.M. Trettel, U. Burghaus, Chemical Physics Letters 590, 146-152, (2013)
0.74	0.34	A. Chakradhar, U. Burghaus, Chemical Communications 50, 7698 - 7701, (2014)
0.74	0.48	Supplemental to N. Sivapragasam, M.T. Nayakasinghe, U. Burghaus, J. Vac. Sci. Technol. 34, 041404, (2016)

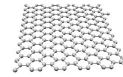
Left hand side

Auger electron spectra of the clean ruthenium support and graphene on that support.

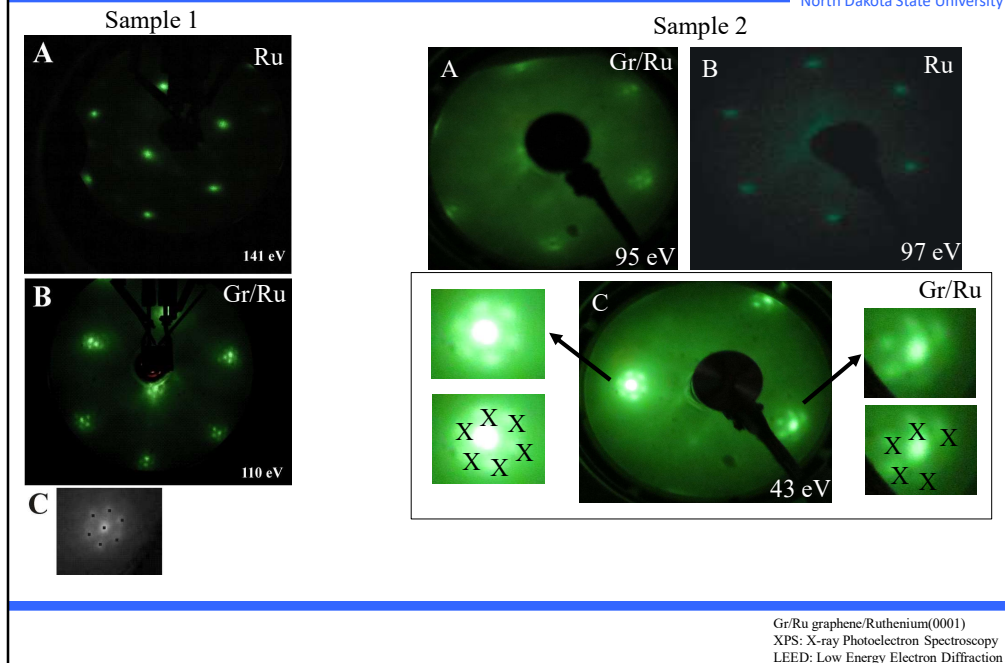
Since Ru and C AES peaks overlap, the p/n peak ratio is used as a characterization.

According to STM works (e.g., see Goodman, et al.) and other spectroscopy the p/n ratios obtained here are characteristic of clean Ru and a single atom thick layer of carbon on it.

LEED - sample characterization



North Dakota State University



Right hand side

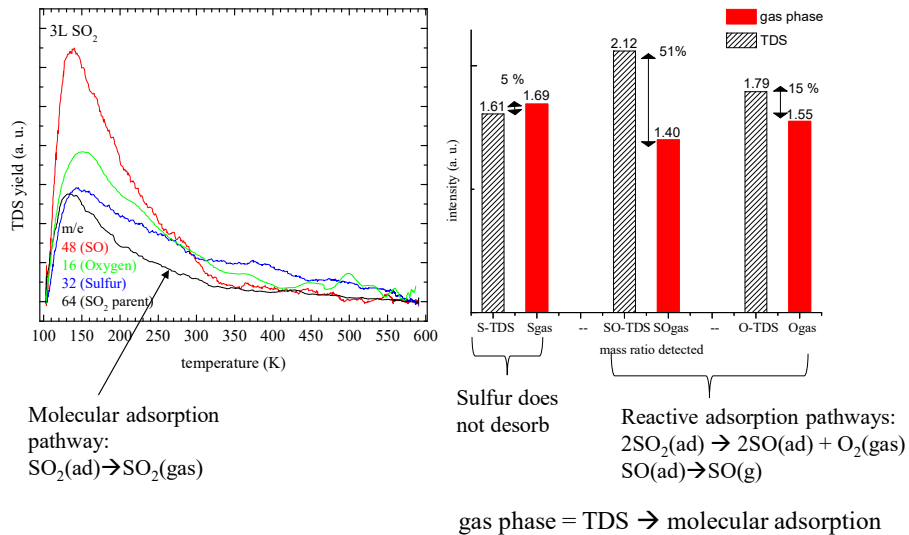
As also discussed in ref. [Effects of surface impurities on epitaxial graphene growth, Valeria del Campo, Ricardo Henríquez, Patricio Häberle, Applied Surface Science 264 (2013) 727-731] obtaining good LEED images of graphene's/ruthenium Moré structure is difficult due to lack of perfect focusing and photographic problems. Having all satellite peak in focus with the same settings of the LEED system was not possible. However, the extra LEED spots surrounding the substrate LEED pattern are evident. A) LEED of graphene at 95 eV, B) LEED of clean ruthenium at 97 eV, C) LEED of graphene at 43 eV, here the sample was rotated by a few degrees, i.e., sample was not parallel to the LEED screen. Highlighted are the satellite spots using the letter "x".

LEED images for two different graphene samples are shown



Multi-mass TDS of SO₂

North Dakota State University



uwe.burghaus@ndsu.edu

Left side

TDS, thermal desorption spectroscopy, curves for different masses.

Right side

Comparison of the SO₂ gas phase fragmentation pattern with the integrated TDS peak areas (/intensities).

Depicted is always the ratio of a given mass to the parent mass of SO₂.

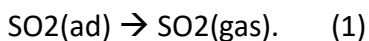
E.g., S-TDS is the ratio of the integrated TDS peak areas of the mass spec. signals for m/e=32 (sulfur) with respect to m/e=64 (parent/molecular SO₂), or S_{gas} is the intensity ratio of m/e=32 (sulfur) with respect to m/e=64 (parent/molecular SO₂) for gas phase SO₂ (detected with the same mass spec.).

Main result:

SO and O TDS signals are larger than the corresponding SO₂ gas phase signal which suggests the decomposition of SO₂ since more SO and O are formed than expected for purely molecular SO₂.

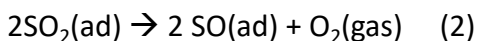
More details:

The parent mass signal for SO₂ at m/e=64 (left side, black curve) must be related to molecular adsorption and desorption of SO₂. Since this signal is detected, we have evidence for the process



A comparison of the TDS signals at various other masses with the corresponding SO₂ gas phase fragmentation pattern measured with the same mass spectrometer allows one to detect none-molecular adsorption/reaction pathways.

SO and O TDS signals are larger than the corresponding SO₂ gas phase signal (i.e., the gas phase fragmentation pattern) which would suggest

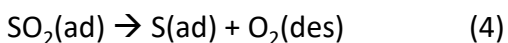


Since all fragments desorb at the same and rather low temperature, a molecular adsorption/desorption pathway for SO seems likely.

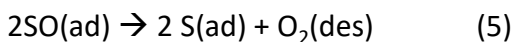
Furthermore, the S TDS signal agrees with SO₂ gas phase fragmentation pattern of sulfur, i.e., sulfur does not desorb up to 600 K.

That TDS result is consistent with sulfur seen on the surface with AES (next slide) after the TDS experiments.

Therefore, another adsorption/reaction pathway must exist that generates sulfur such as



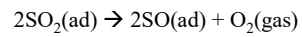
or



AES did not detect adsorbed oxygen after the TDS runs, i.e., O₂ indeed preferentially desorbs rather than forming graphene oxide. The p/n AES ratio of graphene slightly decreased after the TDS experiments, which indicates an increase of carbon on the surface. Thus, graphene seems not to decompose while interacting with SO₂. The increase in carbon likely is caused by our AES system, the micro CMA based AES is rather short. Therefore, carbon desorbs from the filament of the AES electron gun which is in line of sight to the sample. Thus, while collecting AES data some amorphous carbon is deposited on the surface.

Estimating reaction probability for SO₂ decomposition

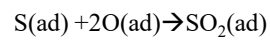
North Dakota State University



$$\eta = \frac{SO^{\text{formed}}}{SO_2^{\text{molecular}}} = \frac{SO_{\text{TDS}} - SO_{\text{gas}}}{SO_{\text{gas}}} \approx \frac{2.12 - 1.40}{1.40} = 0.51$$

$$\eta = 2 \frac{O^{\text{formed}}}{SO_2^{\text{molecular}}} = 2 \frac{O_{\text{TDS}} - O_{\text{gas}}}{O_{\text{gas}}} \approx 2 \frac{1.79 - 1.55}{1.55} = 0.31$$

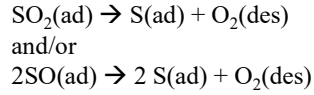
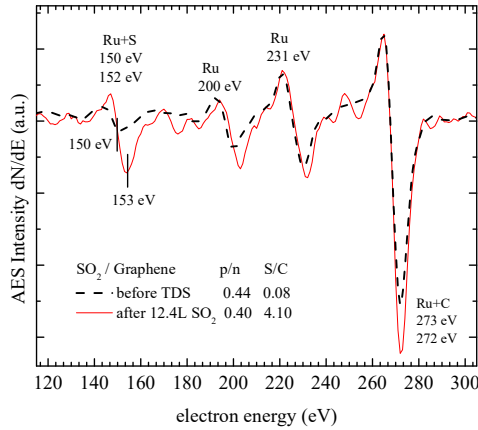
> defect density < 5%



uwe.burghaus@ndsu.edu

Auger after SO₂ TDS

North Dakota State University



$$I_{\text{post}} = \alpha_{\text{Ru}} I_{\text{pr}} + \alpha_{\text{S}} I_{\text{S}}$$

$$\Theta_{\text{S}} = \frac{I_{\text{S}}}{\alpha_{\text{Ru}} I_{\text{Ru}}}$$

$$\Theta_{\text{S}} \approx 0.5ML$$

uwe.burghaus@ndsu.edu

post: intensity after SO₂ adsorption
pr: intensity prior SO₂ adsorption

AES sensitivity factors
 $\alpha_{\text{Ru}} = 0.55$; $\alpha_{\text{S}} = 0.90$

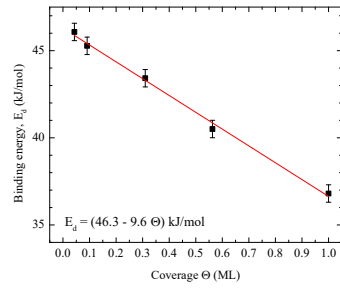
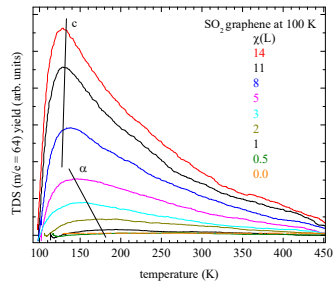
There is a Ru AES peak close to the S AES peak. However, the intensity in the S AES region clearly increases after the TDS experiments. Interestingly, also the Ru+S peak shifts towards the expected sulfur AES peak position consistent with the decomposition of SO₂ seen in the TDS experiments.

The estimate assumes that the Ru signal after the sulfur is adsorbed remains the same as for the clean surface.

That does ignore the attenuation of the Ru signal due to being covered by sulfur. Thus, the Ru signal after S deposition will be a bit smaller than for the clean surface. Thus, I_{post} is underestimated and so is Θ_{S} . The actual S coverage should be larger.

Parent-mass TDS of SO₂

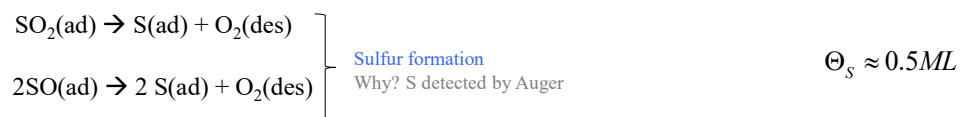
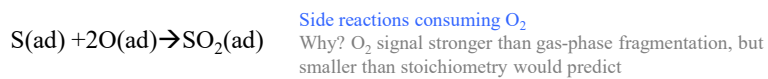
North Dakota State University



uwe.burghaus@ndsu.edu

Proposed kinetics mechanism for SO₂ graphene/Ru - summary

North Dakota State University



uwe.burghaus@ndsu.edu

Proposed electronic mechanism

North Dakota State University

- part of van der Waals interactions from a substrate are transmitted through graphene
- hybridization of substrate and graphene orbitals
- graphene defects as active sites
- charge transfer from dopants to graphene

Current literature suggests as a working **hypothesis** for our project that epitaxial graphene can act as a catalyst due to hybridization of graphene's carbon with the substrate.

uwe.burghaus@ndsu.edu

Possible mechanisms and working hypothesis

For developing a working hypothesis for the proposed projects, one may want to consider possible mechanisms explaining why a carbon-based system may become a catalyst. Searching the literature, several ideas become apparent.

1) Considering molecular adsorption. A few years back the adsorption of water on epitaxial graphene was a focus area.¹⁻⁷ Theoretical works suggested that at least part of van der Waals interactions from a substrate are transmitted through graphene, i.e., the polarization of the substrate can affect surface properties of graphene.⁴ That is not restricted to metallic substrates but, e.g., glass or silica as a substrate also can affect van der Waals type interactions.⁴

2) More important for our projects, for more covalent interactions a different mechanism was recently suggested.^{8,9} In this combined experimental and DFT study, a hybridization of nickel (used as a substrate) and graphene orbitals was proposed to enhance the reactivity for CO adsorption.⁸ Graphene's structure was not altered. Hybridization effects should not be restricted to metallic substrates. Metal substrates are primarily used in many studies so far simply because it's easier to grow graphene on metals. If graphene on non-metallic systems also becomes reactive due to hybridization effects simply needs an experimental verification. First the reactivity can be characterized using kinetics techniques. Next, electronic structure properties become apparent in XPS data.

3) Liquid phase studies usually consider graphene (carbon flakes) not bound to a substrate. In most studies the graphene flakes are functionalized which determines the reactivity. For example, during oxidation of graphene, the sp^2 hybridized carbon of graphene changes to a sp^3 in order to accommodate the oxygen.¹⁰ DFT studies have shown that the oxidation of graphene can form various oxygen containing functional groups: epoxide, hydroxyl, and carboxyl.¹¹ Both the aromaticity and the reactive oxygen containing functional groups in GO can act towards making GO a reactive material. Besides GO other functionalization have been shown to be effective. Many theoretical studies in the literature are devoted to understanding the mechanism by which functionalization modifies the reactivity of graphene. For example, the binding

energy of Pt doubles by N-doping graphene. This DFT study suggests that the nitrogen atoms locally destabilize the delocalized double bond present in graphene.¹² Or, in an experimental study about H₂S oxidation by an N-doped carbon catalyst, it was suggested that nitrogen groups act as Lewis basic sites increasing the local basicity of coadsorbed water which facilitate the dissociation and subsequent oxidation of H₂S.¹³ Examples where a charge transfer from N or S dopands of graphene to adsorbates is invoked (leading to dissociation of the adsorbate) also can be found in the literature.¹⁴

4) Another mechanism is related to defects in graphene. According to a DFT study¹⁵ defects in graphene create C atoms with dangling bonds (i.e. unpaired valence electrons) which enhance graphene's reactivity. In particular, the dissociation of phenol was catalyzed by defects.¹⁵ Experimentally, the defect density of graphene can be manipulated by electron or ion bombardment using a sputter gun, or the electron gun from the Auger or LEED system. That again should be independent of the type of substrate (metal vs. non-metallic) used.

Current literature suggests as a working **hypothesis** for our project that epitaxial graphene can act as a catalyst due to hybridization of graphene's carbon with a metallic or non-metallic substrate. And, a functionalization certainly modifies graphene's electronic structure to become more reactive e.g. by charge transfer.

Uwe Burghaus

**- Surface Chemistry | Het. Catalysis | Nanoscience |
Materials -**

**North Dakota State University, Dept. Chemistry &
Biochemistry**

uwe.burghaus@ndsu.edu

www.uweburghaus.us

<https://www.ndsu.edu/chemistry/people/faculty/burghaus.html>

References

- 1 Burghaus, U., "Adsorption of water on two-dimensional crystals: water/graphene and water/silicatene (short review)" *Inorganics* **4**, 10; <http://www.mdpi.com/2304-6740/4/2/10/pdf> (2016).
- 2 Rafiee, J., Mi, X., Gullapalli, H., Thomas, A. V., Yavari, F., Shi, Y., Ajayan, P. M. Koratkar, N. A., "Wetting transparency of graphene" *Nature Materials* **11**, 217, (2012).
- 3 Shih, C. J., Wang, Q. H., Lin, S., Park, K. C., Jin, Z., Strano, M. S. Blankschtein, D., "Breakdown in the Wetting Transparency of Graphene" *Phys. Rev. Lett.* **109**, 176101, (2012).
- 4 Shih, C. J., Strano, M. S. Blankschtein, D., "Wetting translucency of graphene" *Nat. Mater.* **12**, 866, (2013).
- 5 Raj, R., Maroo, S. C. Wang, E. N., "Wettability of Graphene" *Nano Lett.* **13**, 1509-1515, (2013).

- 6 Chakradhar, A. Burghaus, U., "Adsorption of water on graphene/Ru(0001)—an experimental ultra-high vacuum study" *Chemical Communications* **50**, 7698 - 7701, (2014).
- 7 Chakradhar, A., Sivapragasam, N., Nayakasinghe, M. T. Burghaus, U., "Support effects in the adsorption of water on CVD graphene: an ultra-high vacuum adsorption study," *Chemical Communications* **51**, 11463 - 11466, (2015).
- 8 Elias, D. C., Nair, R. R., Mohiuddin, T. Morozov, S. V., "Control of graphene's properties by reversible hydrogenation: evidence for graphane" *Science* **323**, 610-613, (2009).
- 9 Balog, R., Jørgensen, B., Wells, J., Lægsgaard, E., Hofmann, P., Besenbacher, F. Hornekær, L., "Atomic Hydrogen Adsorbate Structures on Graphene" *J. AM. CHEM. SOC.* **131**, 8744–8745, (2009).
- 10 Vinogradov, N. A., Schulte, K., Ng, M. L., Mikkelsen, A., Lundgren, E., Mårtensson, N. Preobrajenski, A. B., "Impact of Atomic Oxygen on the Structure of Graphene Formed on Ir(111) and Pt(111)" *J. Phys. Chem. C* **115**, 9568, (2011).
- 11 Su, C. Loh, K. P., "Carbocatalysts: Graphene Oxide and Its Derivatives" *Acc. Chem. Res.* **46**, 2275–2285, (2013).
- 12 Groves, M. N., Chan, A. S. W., Malardier-Jugroot, C. Jugroot, M., "Improving platinum catalyst binding energy to graphene through nitrogen doping" *Chemical Physics Letters* **481**, 214-219, (2009).
- 13 Sun, F., Liu, J., Chen, H., Zhang, Z., Qiao, W., Long, D. Ling, L., "Nitrogen-Rich Mesoporous Carbons: Highly Efficient, Regenerable Metal-Free Catalysts for Low-Temperature Oxidation of H₂S" *ACS Catal.* **3**, 862–870, (2013).

14 Wang, Y., Shen, Y., Zhou, Y., Xue, Z., Xi, Z. Zhu, S., "Heteroatom-Doped Graphene for Efficient NO Decomposition by Metal-Free Catalysis" ACS Appl. Mater. Interfaces **10**, 36202–36210, (2018).

15 Widjaja, H., Oluwoye, I., Altarawneh, M., Hamra, A. A. B., Lim, H. N., Huang, N. M., Yin, C. Y. Jiang, Z. T., "Phenol dissociation on pristine and defective graphene" Surface Science **657**, 10-14, (2017).

Conclusions

North Dakota State University

- D₂ TDS: graphene's defect density below 5% ML
- TDS & AES: SO₂ on graphene/Ru(0001)
- SO₂ adsorbs molecularly
- deviations of the gas-phase fragmentation pattern and multi-mass TDS
- SO and O₂ desorbs in SO₂ TDS experiments
- AES revealed adsorbed sulfur after the kinetics experiments

Research presented was supported by ND EPSCoR
ND EPSCoR STEM Solicitation – Seed Award

uwe.burghaus@ndsu.edu

- The adsorption of SO₂ and H₂S on graphene/Ru(0001) were studied by TDS and AES.
- A defect density of the single layer graphene much below 5% of a monolayer was detected by D₂ TDS while synthesizing the samples.
- SO₂ and H₂S adsorb molecularly as well as decomposes.
- Deviations of the gas-phase fragmentation pattern and multi-mass TDS pattern were observed.
- SO and O₂ desorbs in TDS experiments
- AES revealed adsorbed sulfur after the kinetics experiments.