

PROBING CARBONACEOUS SURFACE CHEMICAL AND TOPOLOGICAL HETEROGENEITY BY TEMPERATURE PROGRAMMED PROPANE ADSORPTION/DESORPTION

S. Kwon^{1,2}, *R. Vidic*¹, and *E. Borguet*^{2,3}

¹*Department of Civil and Environmental Engineering,* ²*Surface Science Center and*
³*Department of Chemistry, University of Pittsburgh, 219 Parkman Ave. Pittsburgh, PA 15260*

Introduction

This study reports the adsorption and desorption of a model adsorbent representative of a non polar organic compound (propane) on model carbonaceous surfaces (HOPG), both raw and plasma oxidized, to elucidate the effect of chemical functional groups and surface morphology on adsorption/desorption behavior. This approach can provide a better understanding of the adsorption and desorption characteristics of carbonaceous surfaces that contain chemical and morphological heterogeneity.

Experimental

A 2 mm-thick highly piece of oriented pyrolytic graphite (HOPG), [1] was spliced into several samples about 0.5 mm thick, one of which was used to prepare plasma oxidized HOPG (p-HOPG). Propane (Matheson Tri-Gas, Inc., research grade) was used as supplied. The plasma oxidation was performed for 20 min in a plasma generator (March plasmod, March Inst. Co) with 1 mbar of O₂ pressure and 100 W of power. Raw HOPG was prepared by cleavage in air using scotch tape. Raw HOPG and p-HOPG samples were transferred to an atomic force microscope (AFM).[2] Contact mode imaging was performed with a silicon nitride tip in air at room temperature. Both raw HOPG and p-HOPG samples were installed in a stainless steel ultra high vacuum (UHV) chamber, operating at base pressure of $5 * 10^{-10}$ torr. Total gas pressure was measured with an ion gauge and controller (type 307, Granville-Phillips) and residual gas analysis and leak checking were performed with a quadrupole mass spectrometer (QMS).[3] Samples can be cooled to 88 K with liquid N₂ and resistively heated to 1323 K (1050 °C). K-type thermocouples were spot-welded to a Ta support plate and wedged against the sample. The samples can be rotated 360° around vertical axis under vacuum via a differentially pumped rotatable seal, allowing each sample to be moved toward the opening of the stainless steel mass spectrometer shield. The QMS was fitted with a stainless steel shield to ensure collection of molecules from the sample alone during thermal desorption experiments.[4] The shield

aperture could be repeatedly positioned to within < 1mm of the sample for temperature programmed desorption (TPD) experiments and retracted about 20 mm to allow sample rotation and dosing. After heat treatment to the desired temperature, the sample was typically held at 92 K during dosing. The constant temperature ramping rate, typically 2.5 K/sec, was provided by a computer interfaced (LabView) power supply. Partial pressure and sample temperature signals were monitored via a personal computer equipped with an A/D board controlled by a customized LabView program.

Results and Discussion

Both raw and plasma oxidized HOPG have been imaged by atomic force microscope (AFM), as shown in Figure 1. Oxygen plasma treatment provides a significant amount of pits and defects on the graphite surface, which are shown as darker spots on the image while the raw HOPG reveals a clean and flat surface except for a step (~2.5 nm deep). The defects on plasma treated HOPG vary from ~10 to ~200 nm in diameter, and from ~1 to ~10 nm in depth. It can be concluded that plasma treatment results in the formation of a morphologically heterogeneous surface distinct from the topologically homogeneous raw surface.

The gas evolution profiles following the initial heat treatment of raw HOPG are displayed in Figure 2. Heat treatment leads to desorption of 16, 18 and 44 atomic mass unit (amu) containing species, possibly CH₄, H₂O and CO₂. While all three continue to evolve up to 1073 K (800 °C) heat treatment, the amount decreases significantly for the highest temperature heat treatment of 1323 K (1050°C) (Fig 2.(d)). It can be seen from Figure 2.(d) that there is no re-adsorption over the ~24 hour that elapse between each successive heat treatment because the gas evolution only starts at temperatures higher than previous day's maximum treatment temperature. The heat treatment of plasma oxidized HOPG, not displayed here, showed similar behavior.

Figure 3 shows a series of TPD spectra for propane dosed raw HOPG following heat treatment at various temperatures. A peak appears around 120 K for all cases and saturates at 3L for 673 K (400 °C), 7L for 873 K

(600 °C) and 8L for 1173 K (900 °C) heat treatments, respectively. As the heat treatment temperature increases, it is obvious that the peak height increases for the same exposure level. Figure 4 illustrates the TPD areas, corresponding to relative amount of propane molecules adsorbed at 25 L exposure as a function of heat treatment temperature. The results of Figure 2 suggest that there exist some oxygen and hydrogen containing functional groups on HOPG surface that can be removed by thermal treatment. The result of Figure 3 and 4 suggest that the removal of those functional groups increases the number of accessible adsorption sites for propane molecules. The saturation of the adsorption uptake seen in Figure 4, for $T > 800$ °C (1073 K) suggests that heat treatment at $T \geq 800$ °C is needed to clean the HOPG surface for adsorption applications.

The surface morphology effect on adsorption is depicted in Figure 5, which compares TPD spectra from raw and plasma treated HOPG after 900 °C (1173 K) heat treatment to clean the surfaces. On raw HOPG up to 3 L propane exposure, one peak with a leading edge appears at around 120 K. For plasma oxidized HOPG two peaks at around 175 K and 120 K grow together. With increasing exposure, the higher temperature peak shifts to lower temperatures. The growth of the lower temperature peak with exposure resembles that observed for the raw HOPG except that the peak height is an order of magnitude lower. We believe that such behavior is induced by the defects generated by plasma treatment. These defects provide additional adsorption sites with stronger binding energy. This effect can also be visualized in Figure 6. The TPD areas for the plasma treated HOPG after 900 °C heat treatment are always greater those for the raw HOPG under the same exposure condition. Hence, the capacity of p-oxidized HOPG is

greater than that of raw HOPG. Also, the propane uptake kinetics appears faster.

Conclusion

Oxygen and hydrogen containing functional groups exist on both air cleaved HOPG and plasma oxidized HOPG. They can be removed by thermal treatment. The removal of those groups leads to an increase of adsorption capacity by over two orders of magnitude. It is essential for carbonaceous surface to be treated over 1073 K (800 °C) for all the adsorption sites to be accessible. Oxygen plasma treated HOPG provides greater surface area available for adsorption and stronger binding energy sites. The surface defects induced by oxygen plasma treatment presumably lead to the higher surface area and topologically heterogeneous carbonaceous surface. This study provides insight in the role of surface chemical and topological heterogeneity in the adsorption process on carbonaceous surfaces used in industrial applications.

References

1. Grade SPI-1, SPI Supplies Co.
2. Molecular Imaging.
3. Stanford Research System, AccuQuad 300.
4. Schlichting H and Menzel D. Techniques for Wide Range, High Resolution and Precision, Thermal Desorption Measurements. Surf. Sci. 1993;285:209-218

Acknowledgement

This work is supported by U. S. DOE under Grant No. DE-FG26-98FT40119. We acknowledge Dr. Yufan He for help in obtaining the AFM images

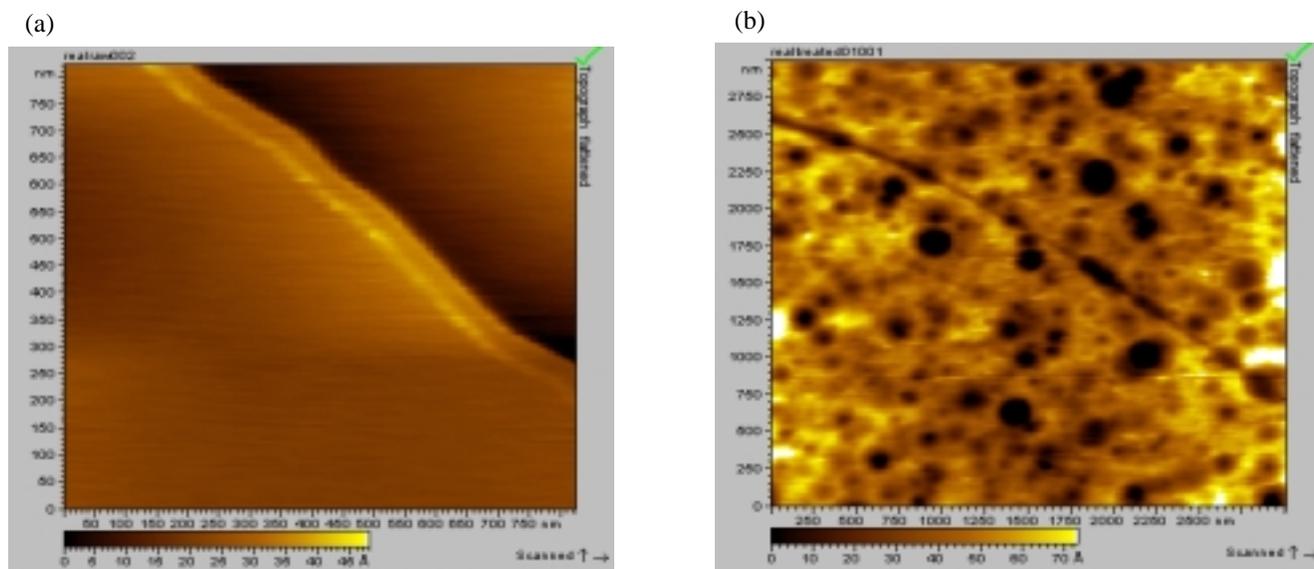


Figure 1. AFM images for (a) raw and (b) O₂ plasma treated HOPG surface.

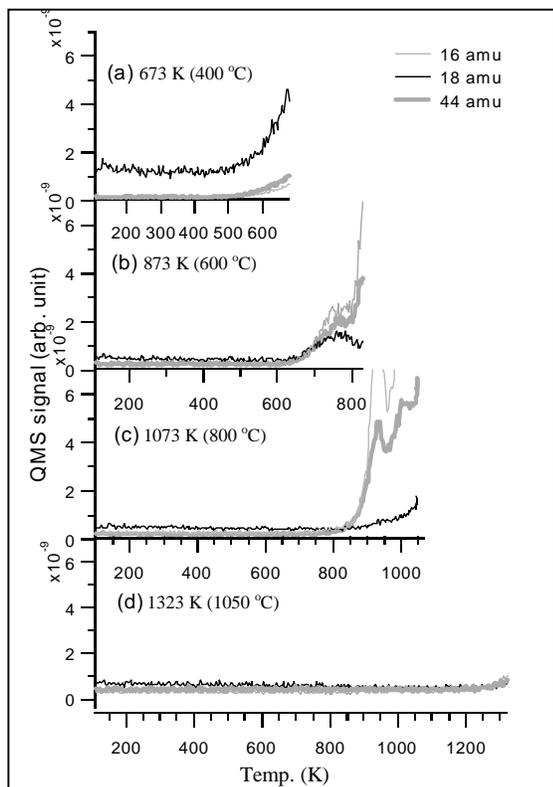


Figure 2. Evolution of masses 16, 18 and 44 amu during initial heat treatment of raw HOPG to (a) 673 K(400°C), (b) 873 K(600°C), (c) 1073 K(800°C), and (d) 1323 K(1050°C). Same scale is used for all y-axes.

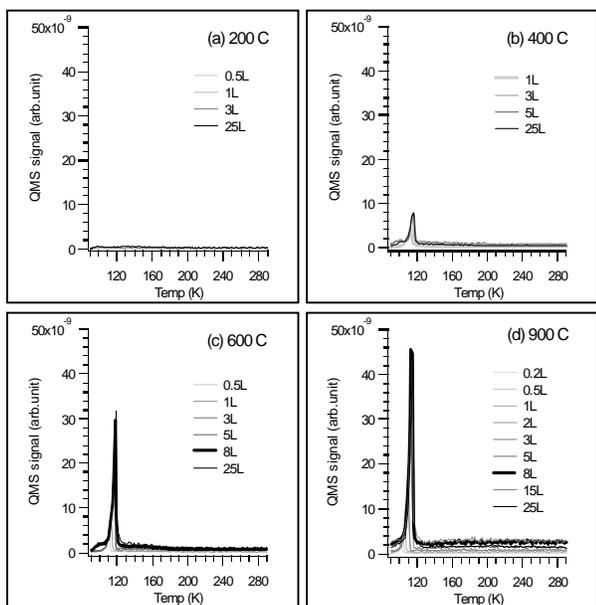


Figure 3. TPD spectra of propane dose on raw HOPG after heat treatment at various temperatures.

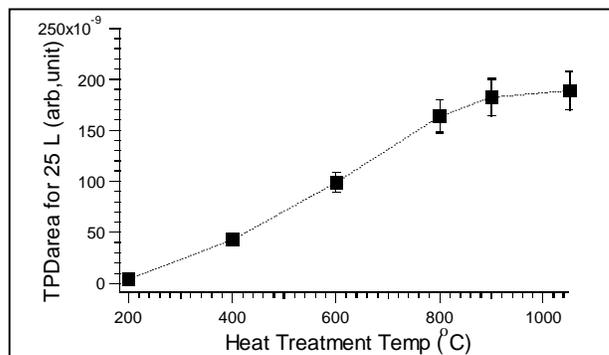


Figure 4. TPD areas from 25 L exposure TPD with increasing heat treatment for raw HOPG.

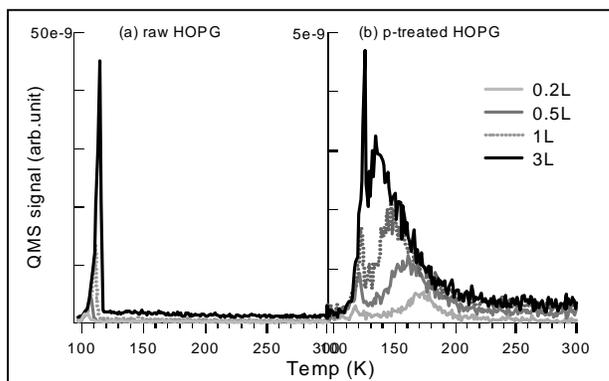


Figure 5. TPD spectra after 900 °C heat treatment for raw HOPG (a) and O₂ plasma treated HOPG (b).

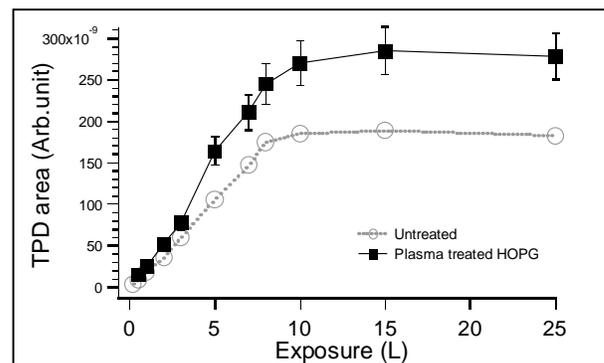


Figure 6. TPD area for both raw and plasma treated HOPG after 900 °C heat treatment.