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STUDIES OF ORGANOPHOSPHORUS NITROGEN AND  
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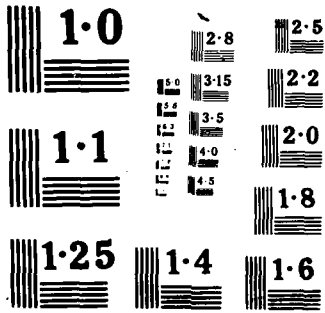
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STUDIES OF ORGANOPHOSPHORUS, NITROGEN AND SULFUR-CONTAINING MOLECULES ON SURFACES

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Final Report

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  This research program encompasses a broadly based surface chemistry study of organophosphorus and organosulfur compounds chemisorbed on and reacting at metal and metal oxide surfaces. Particular attention has been given to phosphine and dimethyl methylphosphonate. The interactions of these molecules with iron, oxidized iron, silica and rhodium have been studied. A thorough surface science study of sulfur adsorption on nickel and its effect on CO chemisorption has also been completed.		

The work accomplished on this project, entitled "Studies of Organophosphorus, Nitrogen and Sulfur-Containing Molecules on Surfaces" is summarized in the following set of eight abstracts which represent papers which are either published or in press from this work. All of these have been submitted as technical reports to ARO. Perhaps the major accomplishment in this work is the successful handling of dimethyl methylphosphonate in the context of ultrahigh vacuum surface science experiments. This work is summarized in abstracts numbers 6 and 8.

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1. R. I. Hegde and J. M. White, "Surface Chemistry of Phosphine on Clean and Oxidized Iron," J. Phys. Chem. 90(1986)2159.

The interaction of  $\text{PH}_3$  adsorbed on clean and oxidized iron at 100 K has been studied by temperature programmed desorption (TPD) and Auger electron spectroscopy (AES). In TPD after  $\text{PH}_3$  adsorption on clean iron, both molecular desorption and dissociative processes are evident. On oxidized iron, the dissociation of  $\text{PH}_3$  is inhibited. Co-adsorption of  $\text{D}_2$  and  $\text{PH}_3$  leads to no detectable deuterium incorporation in the desorbing phosphine, but all the isotopic forms of molecular hydrogen desorb in relatively large amounts. Pre-adsorbed  $\text{PH}_3$  inhibits  $\text{D}_2$  adsorption, while post-dosed  $\text{PH}_3$  not only displaces  $\text{D}_2$  but also changes its desorption peak shape. Compared to clean Fe, adsorption of  $\text{D}_2$  is strongly inhibited both on oxidized and  $\text{PH}_3$ -covered oxidized iron surfaces at 100 K.

2. E. L. Hardegree, Pin Ho and J. M. White, "Sulfur Adsorption on Ni(100) and Its Effect on CO Chemisorption. I. TDS, AES and Work Function Results," Surface Sci. 165(1986)488.

The adsorption of  $\text{H}_2\text{S}$  on Ni(100) at 300 K was investigated. Adsorption is dissociative and proceeds via a mobile precursor, with sulfur strongly chemisorbed and hydrogen desorbing both during the dose and upon subsequent heating. Chemisorbed sulfur causes an increase in surface work function due to charge transfer of about 0.04 e from nickel to sulfur. The adsorption of CO at 95 K was studied on the sulfur-pre-dosed surface using AES, TDS and work function change measurements. Evidence is presented for steric and relatively short-range ( $\sim 4\text{\AA}$ ) electronic effects of S on CO. One sulfur blocks two high-temperature ( $\beta_2$ ) CO sites by steric (site-blocking) effects. In the presence of sulfur, CO redistributes into several lower-temperature desorption states, some of which exist on regions of bare Ni, and some within sulfur domains. At a sulfur coverage of 0.40 ML, a new CO state at 140 K was observed which, unlike the other CO states, caused a slight decrease in the surface work function. The behavior of this state is explained in terms of reduced back-donation from the metal due to close association of the CO with sulfur. Several proposed modes for sulfur's action are evaluated on the basis of the data. These include steric effects, a through-space electrostatic potential, and a through-metal electronic effect involving density of state changes.

3. Pin Ho, E. L. Hardegree, and J. M. White, "Sulfur Adsorption on Ni(100) and Its Effect on CO Chemisorption. II. UPS and XPS Results," Surface Sci. 165(1986)507.

The adsorption of CO on sulfur-pre-dosed Ni(100) at 95 K was studied using ultraviolet and X-ray photoelectron spectroscopies. For sulfur coverages below 0.22 ML, CO ( $\beta_2$  and  $\alpha$ ) adsorbed predominantly on regions of bare Ni, with  $\alpha$  induced by repulsive CO-CO interactions. For  $\theta_s > 0.22$ ,  $\alpha$  and  $\beta_1$  CO adsorbed predominantly within the sulfur domains, and exhibited a reduction in Ni-CO backbonding. By  $\theta_s = 40$ , a weakly bound CO state formed (denoted here as  $\sigma$ ). The close association of  $\sigma$  CO with sulfur resulted in greatly reduced (or nonexistent) backbonding and poor final state relaxation

from the metal.

4. R. I. Hegde and J. M. White, "Chemisorption and Decomposition of  $H_2S$  on Rh(100)," J. phys. Chem. 90(1986)296.

The chemisorption and decomposition of  $H_2S$  adsorbed on Rh(100) at 100K have been studied by thermal desorption and Auger electron spectroscopy. Hydrogen sulfide exposure to clean Rh(100) leads to both molecular desorption and dissociative processes upon heating. On sulfur-covered rhodium, there is less decomposition of  $H_2S$ . The adsorption of  $H_2S$  at 300 K is completely dissociative and hydrogen desorbs during exposure. Preadsorbed D(a) does not alter the desorption energetics of  $H_2S$ . Coadsorption of D and  $H_2S$  leads to no detectable deuterium incorporation in desorbing hydrogen sulfide but the isotopic forms of molecular hydrogen all desorb in relatively large amounts. Preadsorbed D(a) inhibits the decomposition of  $H_2S$ . Postdosing  $H_2S$  does not displace D(a) from the surface at 100 K but does shift the deuterium desorption to significantly lower temperatures.

5. Rama I. Hegde and J. M. White, "Interaction of  $PH_3$  Coadsorbed with  $H_2$ ,  $D_2$ ,  $O_2$  and  $H_2O$  on Rh(100)," Surface Sci. 157(1985)17.

The coadsorption of  $PH_3$  with  $H_2$ ,  $D_2$ ,  $O_2$  and  $H_2O$  on Rh(100) has been studied using temperature programmed desorption (TPD), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). The adsorption and molecular desorption of  $PH_3$  is not affected by preadsorbed  $H_2$ ,  $D_2$  and  $O_2$ . Preadsorbed  $PH_3$  blocks  $H_2$  desorption sites while postdosed  $PH_3$  displaces  $H_2$  ( $D_2$ ) from the Rh(100). When D<sub>2</sub> and  $PH_3$  are coadsorbed, no D appears in desorbed phosphine. Preadsorbed O<sub>2</sub> reduces the amount of  $H_2$  desorption (from  $PH_3$  decomposition) and increases the  $H_2$  desorption temperature. There is also some reaction between O(a) and H(a) to form water. Preexposure to  $H_2O$  decreases the extent of  $PH_3$  adsorption and of  $PH_3$  decomposition.

6. R. I. Hegde, C. M. Greenlief and J. M. White, "The Surface Chemistry of Dimethyl Methyl Phosphonate (DMMP) on Rh(100)," J. Phys. Chem. 89(1985)2886.

The adsorption of dimethyl methyl phosphonate (DMMP) has been studied on clean and carbon-covered Rh(100) surfaces. Temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES) and work function change ( $\Delta\phi$ ) measurements were used to characterize the adsorbed layer as a function of temperature. At 100 K the DMMP adsorbed into two states, a monolayer phase and a multilayer phase which were distinguishable by TPD and spectroscopy measurements. For one monolayer of DMMP on carbon-free Rh(100), between 60 and 70% decomposes upon heating, leaving carbon, phosphorus and oxygen on the surface. On carbon-covered Rh, the decomposition of DMMP is strongly inhibited. On carbon-free Rh, there are two distinct molecular DMMP desorption peaks at 210-225 and 200 K (monolayer and multilayer) with first-order desorption energies of 13.8 and 8.6

kcal/mole, respectively. On the C-covered surface, the higher temperature DMMP desorption peak shifts to slightly lower temperature. XPS of multilayer and monolayer DMMP indicate some dissociative adsorption at 100 K. UPS of multilayer and gas phase DMMP are compared. A bonding configuration of DMMP to the Rh(100) surface is proposed.

7. R. I. Hegde, J. Tobin and J. M. White, "Surface Chemistry of Phosphorus-Containing Molecules: I. Interaction of  $\text{PH}_3$  with Rh(100) and the Effect of Preadsorbed Phosphorus," *J. Vac. Sci. Technol.* A3(1985)339.

The interaction of  $\text{PH}_3$  with Rh(100) has been investigated using temperature programmed desorption spectroscopy, Auger electron spectroscopy, low energy electron diffraction and work function change measurements. A mobile precursor state is involved in the adsorption kinetics at 100 K. The overlayer is saturated after an exposure of 3 L, at which point the work function has decreased by 1.2 eV, indicating adsorption through the phosphorus atoms. Heating the crystal above 100 K desorbs molecular  $\text{PH}_3$  and  $\text{H}_2$  and leaves adsorbed phosphorus atoms on the surface. The  $\text{PH}_3$  thermal desorption spectra show a coverage-dependent adsorption energy associated with repulsive lateral interactions between the adsorbed molecules. There are two thermal desorption states of hydrogen, one of which is characteristic of hydrogen on clean Rh(100). Preadsorbed phosphorus atoms partially passivate the surface, preventing  $\text{PH}_3$  decomposition until higher temperatures are reached. Preadsorbed phosphorus also reduces the capacity of the surface for  $\text{H}_2$  adsorption, but does not alter the activation energy for  $\text{H}_2$  desorption.

8. M. A. Henderson, T. Jin and J. M. White, "A TPD/AES Study of the Interaction of Dimethyl Methylphosphonate with  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{SiO}_2$ ," *J. Phys. Chem.* (in press).

The interaction of dimethyl methylphosphonate (DMMP) dosed at 170 K onto  $\text{SiO}_2$  and  $\alpha\text{-Fe}_2\text{O}_3$ , was studied using temperature programmed desorption (TPD) and Auger electron spectroscopy (AES). On dehydrated  $\text{SiO}_2$  there was no DMMP decomposition and there were two DMMP TPD peaks, a multilayer state at 200-210 K and a monolayer state at 75 K. On hydrated  $\text{SiO}_2$ , no more than 10% of a monolayer decomposed and the only detectable TPD products were methylphosphonate (MP) and methanol. On clean  $\alpha\text{-Fe}_2\text{O}_3$ , multilayer DMMP was observed but no molecular peak corresponding to the monolayer. Decomposition led to  $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{HCOOH}$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$  and an adsorbed phosphate species. The presence of the phosphate species did not completely inhibit the decomposition of subsequent doses of DMMP even after saturation of the AES P(114)/Fe(703) signal ratio at 0.45 to 0.55. The AES P(114)/Fe(703) signal ratio decreased at temperatures above 600 K. Migration of the phosphorus to an iron oxide - phosphate phase below the surface is proposed to explain the continued DMMP decomposition.



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