

9 Summary

This thesis focuses on the research of the adsorption of 1,4-dioxane and 1,3,5-trioxane on a Ag(110)-surface. No change from the stable chair to boat configuration could be noticed with both molecules. The HREELS-losses are consistent with the IR-vibrations of the gaseous molecules.

1,4-dioxane adsorbs and desorbs on the Ag(110)-surface without decomposition while 1,3,5-trioxane decomposes partially. Different research methods have shown that the fragmentation is not only a result of thermal energy. The molecules will be fragmented spontaneously when impinging on the surface. The data also indicate that there is some molecular decomposition to carbon, oxygen, carbon dioxide, carbon monoxide, water, hydrogen, formiat, and carbonat. Formiat and carbonat are not directly formed by the spontaneous fragmentation of trioxane but by subsequent surface reactions of the primary fragments. Formiat is probably the product of the hydrogen decomposition of H_2CO_2 and thermal energy; carbonat is the product of the reaction of carbon dioxide with oxygen.

In many cases atomic oxygen is responsible for the catalytic activity of organic molecules on the silver surface, such as in the 1,3,5-trioxane/Ag(110)-system. The oxygen concentration on the surface is very low because it subsequently reacts with the adsorbed molecules. The presence of oxygen can be proven indirectly by the composition of carbonat. From the HREELS experiments it can be concluded that the development of (oxygen-) reaction centers depend also on the supply of thermal energy. It leads to a stronger fragmentation if more trioxane is offered and therefore new losses within the HREEL spectrum appear.

Strong intermolecular interaction can be noticed between the different adsorbed molecules which are mainly caused by the polar formiat and carbonat. Consequently, all adsorbed molecules have a higher desorption temperature. The trioxane of the monolayer develops two different phases: Most of the trioxane molecules desorb with an activation energy of 56 kJ/mol; the trioxane molecules in the neighborhood of the fragments desorb, however, with an appreciably higher activation energy of about 64 kJ/mol.

In comparison, the desorption activation of 1,4-dioxane/Ag(110) system is only 54 kJ/mol. With both molecules this bonding can be explained by van der Waals forces or interaction with merely small chemical contributions. The interaction with the surface probably occurs via the oxygen atoms since both adsorbed ethers are positively polarized.

Both molecules adsorb without long-range order and preferential orientation. The results indicate a Volmer-Weber growth mechanism for both systems. The NEXAFS study of the 1,4-dioxane in the submonolayer range suggests a relatively parallel orientation of the carbon plane of the molecule with respect to the surface. The sticking probability of trioxane on Ag(110), compared with other cyclic ethers, is very low: the saturation of the monolayer requires an exposure of about 85 L; in contrast, the monolayer of trioxane on Cu(111) is saturated at 6 L, of 1,4-dioxane on Ag(110) at 7 L and of 1,4-dioxane on Pd(111) after 4 L exposure. It seemed that a certain orientation with respect to the surface is essential for successful adsorption, even more for the first impinging molecules, because the sticking probability increases with the population of the surface. The large variety of different fragments makes it difficult to exploit NEXAFS-experiments to gain information on the trioxane/Ag(110)-system.