The interactions of thiophene with polycrystalline UO$_2$

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Abstract

We have studied the adsorption and desorption of thiophene on polycrystalline UO$_2$ as function of coverage, over the temperature range 100–640 K, using X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD) and electron stimulated desorption (ESD). Thiophene is found to adsorb molecularly on stoichiometric UO$_2$. C 1s and S 2p XPS spectra are measured at different thiophene exposures and at different temperatures; they show no evidence for the presence of dissociation fragments, confirming that thiophene adsorbs and desorbs molecularly on a polycrystalline stoichiometric UO$_2$ surface. The variation of the S 2p and C 1s intensity as function of exposure, together with ESD measurements of O$^+$ as function of exposure, can be connected to the growth mode of a thiophene film on UO$_2$; the thiophene film converts from a flat-lying configuration to an inclined structure as coverage increases. The effects of X-rays, UV, and electron irradiation on thiophene films have been studied in two different coverage regimes, monolayer and multilayer. Irradiation leads to a modification of thiophene films, and appreciable concentrations of species stable to 640 K are present on the surface for both regimes. The XPS results suggest that irradiation induces polymerization and oligomerization, as well as formation of thiolates and dissociation fragments of thiophene. The adsorption and reactivity of thiophene on defective UO$_2$ surfaces have also been studied. The O vacancies and defects in the oxide surface cause cleavage of C–H and C–S bonds leading to the dissociation of thiophene at temperatures as low as 100 K. These results illustrate the important role played by O vacancies in the chemistry of thiophene over an oxide surface.
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1. Introduction

A crucial step in petroleum refining before catalytic cracking or reforming is the removal of sulfur from the hydrocarbon feeds via hydrodesulfurization (HDS), to prevent poisoning of the downstream catalysts [1]. Sulfur impurities have a negative impact on the environment: they degrade air quality by forming sulfur oxides (SO_x) during combustion of fuels [2]. New environmental regulations emphasize the importance of more efficient technologies for removing sulfur from oil [3].

Sulfur is typically found in crude oil in the form of thiols, sulfides, and thiophenes [4]. Thiophene and its derivates are the most difficult of these compounds to desulfurize because of their aromatic stability ($\sim85\,kJ\,mol^{-1}$ for thiophene) [4]. Thiophene is an aromatic molecule with π-electron density below and above the plane of four carbon atoms, and lone-pair electrons on sulfur. The most important step of the HDS process, namely, the C–S bond cleavage, is still not completely understood. Important prerequisites for an improved understanding are the knowledge of the initial mode of bonding of thiophene to the surface, the determination of the steps leading towards dissociation of the ring, and the identification of surface intermediates after the desulfurization step. Thus a key step of the reaction would be the weakening of the aromatic π bonding upon adsorption on the surface.

The most widely used catalyst in hydrodesulfurization reactions consists of a mixture of cobalt and molybdenum sulfide on an γ-alumina support [1,5,6]. However, efforts are made to search for new and more efficient HDS catalysts (so-called deep hydrodesulfurization).

Various studies have focused on the chemistry of thiophene over catalytically active transition metals [7–24], metal sulfides [1,9,25,26], and oxide supported catalysts [27–30]. On transition metal surfaces, reasonably strong bonds to the surface are indicated in most cases, as thiophene is found not to desorb molecularly from the surface, but rather

to dissociate upon heating. In some cases dissociation begins at temperatures as low as 100 K, e.g., Fe(1 0 0) [12] and Ni(1 0 0) [14]. For Fe(1 0 0) [12] and Ni(1 1 1) [24], the surface causes selective dehydrogenation which leads to thiophene polymerization. On the surfaces Cu(1 0 0) [15], Cu(1 1 1) [17], Ru(0 0 0 1) [19] and Ag(1 1 1) [22], intact molecular desorption is observed from the monolayer. For Mo(1 1 0) [7,9] or Mo(1 0 0) [8], thiophene decomposition to S and C_xH_y fragments is observed at temperatures below 300 K. Mo and MoS_x nanoparticles on Au(1 1 1) induce dissociation of thiophene [26]. In contrast, on alumina supported Mo sulfide catalysts [29,30], thiophene is weakly chemisorbed. In spite of the use of oxides as catalysts/absorbents in HDS operations [4], little is known about the fundamental chemistry of thiophene on pure and well-defined oxide surfaces [31,32]. On a polycrystalline ZnO surface, thiophene is weakly chemisorbed, and mostly desorbs at temperatures below 250 K [31]. A very small fraction of the adsorbed thiophene that interacts with O-unsaturated Zn sites is decomposed [31]. Previous studies show that on high surface area γ-Al_2O_3 powders, thiophene interacts only weakly with the substrate [32]. However, TiO_2 supported Mo catalysts exhibit higher HDS activity than γ-Al_2O_3 supported Mo [33]. Hence a clear picture of the adsorption of thiophene on surfaces has not yet emerged from the experimental investigations.

There are large stockpiles of depleted uranium stored in the US and it would be desirable to use this material for a positive purpose. New interest has arisen recently in the possibility of using depleted uranium in catalysts for various applications. Uranium oxides (e.g., UO_2) display catalytic activity for the oxidative destruction of volatile organic compounds (VOCs) such as butane, benzene, chlorobenzene, and other chlorine containing molecules [34,35]; UO_2 has also been used as a catalytic support for steam reforming of methane [36]. Surface defects on single crystals of UO_2 have been shown to influence the surface chemistry [37,38]. Recently,