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Molecular beam scattering of CO on iron oxide clusters supported on graphite (HOPG)

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Abstract

The adsorption dynamics of CO has been studied by measuring adsorption probabilities by means of the molecular beam scattering technique. Iron has been vapor deposited on ordered pyrolytic graphite (HOPG) with the vacuum chamber at a base pressure below 3×10^{-10} mbar. However, the Fe clusters partially oxidize, according to Auger electron spectroscopy (AES). Indications for a transition from two-dimensional to three-dimensional cluster growth modes with increasing Fe exposure have been obtained by AES and thermal desorption spectroscopy (TDS). The initial adsorption probabilities, S_0, decrease with increasing impact energy and are systematically larger for larger clusters, consistent with the capture-zone model (CZM) and molecular, non-activated adsorption. S_0 initially increases with adsorption temperature, T_s, and decreases above $T_s = 100$ K. The latter is not fully consistent with the simplest version of the CZM. The coverage dependence of the adsorption probabilities obeys the Kisliuk precursor model, as expected in the framework of the CZM.

Keywords: Adsorption dynamics; CO; Iron oxides; Nanoparticles; Graphite; HOPG; TDS; Molecular beam scattering

1. Introduction

Oxidized and metallic iron clusters as well as thin films are pertinent for a variety of applications [1,2] including catalysis [3–8], magnetic sensing [9], data storage [10], spintronics, as well as biological systems [11,12]. At most reaction conditions small iron particles readily oxidise, forming iron oxide clusters. For example, in the plume of coal combustion plants Fe_2O_3 particles have been identified as a component of particulate matter which may have serious implications for human health [13]. Fly ash can contain nanometer-sized iron oxide particles [14]. These particles interact with typical combustion gases such as CO, O_2, CO_2, and NO. Therefore, it appears interesting to characterize the adsorption kinetics and dynamics of CO with iron oxide [15] particles supported on graphitic systems. Furthermore, iron oxide clusters are efficient catalysts for a variety of reactions including CO–NO conversion [5], as well as the decomposition of CO_2 [7] and chlorinated hydrocarbons [8].

We are aware of projects about Fe cluster growth on highly ordered pyrolytic graphite (HOPG) [16,17], carbon nanotubes [18], Si(1 1 1) [19], sapphire [20], and platinum single crystals [21], as well as studies on Fe films [1,22–24] and a few ultra-high vacuum (UHV) surface science projects on Fe [25,26]/Fe oxide nanoparticles [27–30]. According to scanning electron microscopy (STM) [31] data, Fe clusters preferentially occupy terrace edges even at room temperature on HOPG. After annealing the sample to 800 K, only step edges were occupied. The growth is characterized by a narrow particle size distribution centred at ~6 nm. In a transmission electron microscopy study [28,32] it has been shown that small (<8 nm) Fe nanoparticles completely oxidize in O_2 ambient forming a polycrystalline phase. For larger particles, a single crystalline Fe core is present which is encapsulated by polycrystalline iron

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oxides. Similarly to results on single crystals [29,33,34] mixed Fe_2O_3 (maghemite)/Fe_3O_4 (magnetite) oxides form. Unique features of Fe and Fe oxide nanoclusters also have been revealed theoretically. For example, unusually large binding energies of N_2 have been observed [35]. Furthermore, gas phase scattering projects on Fe clusters concerning Fe cluster oxidation [30] and CO adsorption/oxidation [36] on FeO_x have been conducted. In a previous study we characterized the effect of the oxidation state on the adsorption kinetics (by TDS – thermal desorption spectroscopy) and dynamics (by molecular beam scattering) by annealing Fe clusters in oxygen [15]. The prior project focused on kinetics experiments. Two CO TDS features have been seen at 150 K and 250 K and were assigned to CO adsorption on Fe^{3+} and Fe^{2+} cation adsorption sites indicating formation of Fe_2O_3 and Fe_3O_4. Besides this kinetic structure activity relationship the effect of the oxide stoichiometry on the energy transfer processes (i.e., on adsorption probabilities) was negligible. Thus, while studying the adsorption dynamics it is not required to perfectly control the oxidation state of the iron oxide clusters.

Although a large number of kinetic studies have been conducted on clean HOPG [37–40] only few molecular beam scattering projects have been published. For example, the oxidation and patterning of HOPG by an effusive atomic oxygen beam [41], methane decomposition on platinum leading to a graphitic layer on the surface [42], He atom scattering on CO/Fe(1 1 1) [43], and effusive beam scattering of large hydrocarbons to form organic films [44] have been studied; supersonic beam scattering of small molecules such as Xe for testing molecular dynamics simulations have been conducted as well [45,46]. Still, rather few results of molecular beam scattering studies have been published on supported model catalysts (see e.g., Refs. [4,47–50]). We are not aware of molecular beam projects conducted on Fe or iron oxide clusters. However, dynamics parameters such as adsorption probabilities are part of every kinetic model of related surface reactions.

In this report we focus on the adsorption dynamics, including particle size effects.

2. Experimental procedures

The measurements have been conducted by a home-built, triply-differentially pumped supersonic molecular beam system [51]. The beam is attached to a scattering chamber (base pressure below 3×10^{-10} mbar) which contains a shielded mass spectrometer, an Auger Electron Spectroscopy system (AES), and a home-built metal evaporator. Nanoparticles are formed by vapor deposition of Fe (from Goodfellow, 99.95% purity) by means of resistively heating a Fe filament (diameter 0.1 mm). The equivalent Fe coverage has been estimated from AES and CO-TDS measurements. The impact energy, E_i, of the CO molecules could be varied within (0.12–0.7) eV by seeding 3% CO in He, combined with a variation of the nozzle temperature within 300–650 K (see Ref. [51]). The adsorption isotherms (King and Wells curves [52]) are smoothed while conserving the shape of the curves. The reading of the thermocouple has been calibrated *in situ* by TDS measurements of condensed alkanes.

3. Presentation of the results

3.1. Auger electron spectroscopy data

Fig. 1 shows AES spectra as a function of Fe exposure at 300 K. Besides the Fe AES lines (at 603, 656, 710 eV) and the carbon line of the support (at 280 eV) an oxygen signal (at 517 eV) is also seen (see the inset of Fig. 1). The peaks are shifted by ~10 eV due to charging of the support with respect to reference spectra [53]. Throughout the project, the scattering chamber has been opened several times in order to clean the sample by the Scotch tape method, since it turned out that the iron cannot entirely be removed from the HOPG support by annealing/flashing (up to 1200 K). The averaged stoichiometry of the cluster ensemble can be estimated by $x = \text{AES} - O_{506}/\text{AES} - Fe_{703}$ from AES data and is within the range of 0.17–0.22 for the data shown in Fig. 1. As mentioned above, the adsorption dynamics is not affected by the FeO_x cluster stoichiometry [15].

Fig. 2A depicts the Fe_{703} AES intensities (triangles) and the CO TDS peak areas (squares) vs. iron exposure time, χ_{Fe}. The intensities need not to be normalized, since only the shape of the curves is important. The surface has been saturated with CO for the TDS experiments. Both quantities (Fe AES and CO TDS intensities) increase linearly with

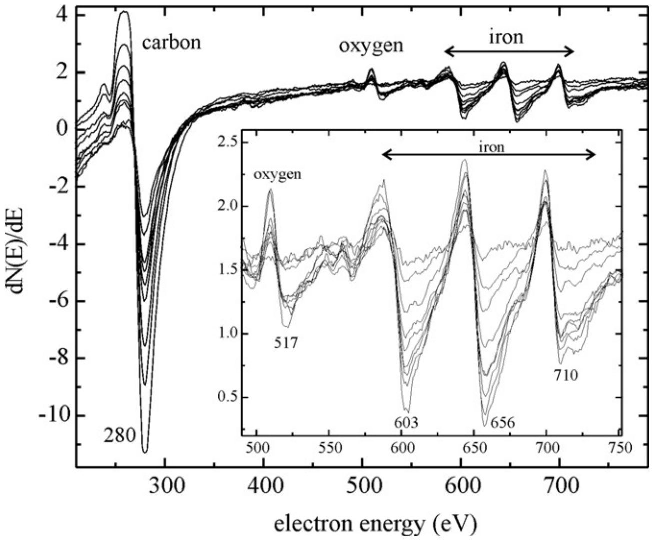

Fig. 1. Auger electron spectroscopy (AES) data of the FeO_x/HOPG system and for different iron exposures $\chi_{Fe} = 0.5$; 1.5; 2.5; 3.5; 4.5; 5.5; 6.8; 8.5 in min at a surface temperature of $T_s = 300$ K. The inset shows an O–Fe region. The averaged cluster stoichiometry (see text) of the data shown here is in the range of 0.17–0.22. (AES parameters: 2 keV, 5 V modulation).