



Methanol adsorption in carbon nanotubes

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Abstract

Presented are thermal desorption spectroscopy (TDS) data of methanol, *n*-pentane, and methanol/*n*-pentane co-adsorbed on carbon nanotubes (CNTs) supported on silica. Whereas alkane TDS indicates three different adsorption sites (external, groove, internal), in agreement with earlier studies, only two structures are present in methanol (MeOH) TDS consistent with the dominance of strong MeOH–MeOH hydrogen bonding. However, the co-adsorption data provide evidence for MeOH adsorption on interior sites.

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1. Introduction

A large number of possible applications for carbon nanotubes (CNTs) have been explored since their discovery. Frequently approaches are devoted towards material science applications, such as additives for composite materials, molecular sensors, the capture of toxic compounds, H₂/Li storage, as well as applications in nanoelectronics. Comparatively little attention has been paid to applications in heterogeneous catalysis by means of ultra-high vacuum (UHV) surface chemistry techniques; gas–nanotube interactions are rather unexplored [1–5]. However, the use of CNTs as a new class of supports for fuel cell catalysts [6] and the Fischer–Tropsch synthesis [7] has been demonstrated.

Direct liquid fuel cells can be regarded as green chemistry, providing alternative means of electricity production based on renewable energy sources. The most promising fuel cells are based on methanol (MeOH), which is safe, renewable, and easily storable [6]. Crucial to the operation of fuel cells is the adsorption of the fuel (methanol) on the electrode surface. A major problem is anode–cathode cross-over of the liquid. A more efficient catalyst to oxidize more

liquid is therefore desirable. Nanotube-based catalysts are promising; prototypes already show superior performance [6]. An improvement in these applications requires detailed knowledge of the liquid/gas–nanotube interaction. Furthermore, studying the interactions of hydrocarbons with carbon surfaces has implications for lubrication [8] and self-assembly in nanoelectronics [9] applications. Another motivation (in fundamental research) for studying methanol/graphite interactions is related with the detection of MeOH on interstellar dust grains. Carbonaceous surfaces are considered a good model system [10].

The adsorption and decomposition of MeOH has been studied extensively on metal surfaces [11], alloys [12], and metal oxides [13]. However, rather few surface chemistry studies with methanol have been conducted on graphitic systems [2,14,15]. Besides a reactivity screening of ‘bucky paper’ (thick multi wall CNTs layers) including (one) methanol TDS curve [2], we are not aware of UHV surface chemistry projects about alcohol–CNTs interactions. Although 1st-order kinetics has been observed for methanol adsorption on other surfaces, [12] the desorption kinetics was complicated on HOPG (highly oriented pyrolytic graphite) by hydrogen bonding between adjacent methanol molecules leading to slight deviations from 1st-order kinetics.

Before studying MeOH adsorption on supported CNTs (Pt and Ru nanoclusters have shown the best results for

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fuel cells) it is crucial to characterize clean CNTs in order to stimulate a mechanistic understanding. We present methanol thermal desorption spectroscopy (TDS) on a CNT monolayer supported on silica. To characterize the sample, TDS data of *n*-pentane have been collected which leads to ‘fingerprint’ curves indicating, for example, whether the ends of the nanotubes are open or closed [16]. In addition, MeOH and *n*-pentane co-adsorption experiments have been conducted, following the methodology in Ref. [1], which provided strong evidence that methanol occupies internal adsorption sites.

2. Experimental procedures

The experiments have been conducted with a standard UHV system including a shielded mass spectrometer. The TDS setup is identical with the one described in Ref. [17]. All gas exposures are given in Langmuir (1 L = 1 s at 1×10^{-6} Torr); a heating rate of 1 K/s has been used. The single-walled CNTs (based on HiPco powders from Carbon

Nanotechnologies Inc.) were dispersed in aqueous sodium dodecyl sulfate (SDS) and deposited on a 10×10 mm silica wafer by the drop-and-dry technique [4,18]. In order to clean off the SDS, the sample has been annealed at 600 K in a N_2 stream for 30 min. Scanning electron microscopy revealed the presence of a monolayer of CNTs covering entirely the wafer [4]. MeOH and pentane have been cleaned by multiple freeze-pump-thaw cycles.

3. Data presentation and discussion

Fig. 1 summarizes the sample characterization; *n*-pentane TDS as a function of exposure, χ (L), is shown in the lower panel for small, and in the upper one for large exposures. The curves agree with published data from Yates and co-workers [1,16]. Based on infrared spectroscopy data and the determination of filling factors [1,16], the structures could be assigned to the adsorption of the alkane on internal (A-peak), groove (B), and external (C) sites. Thus, the CNT sample is clean and the tube ends

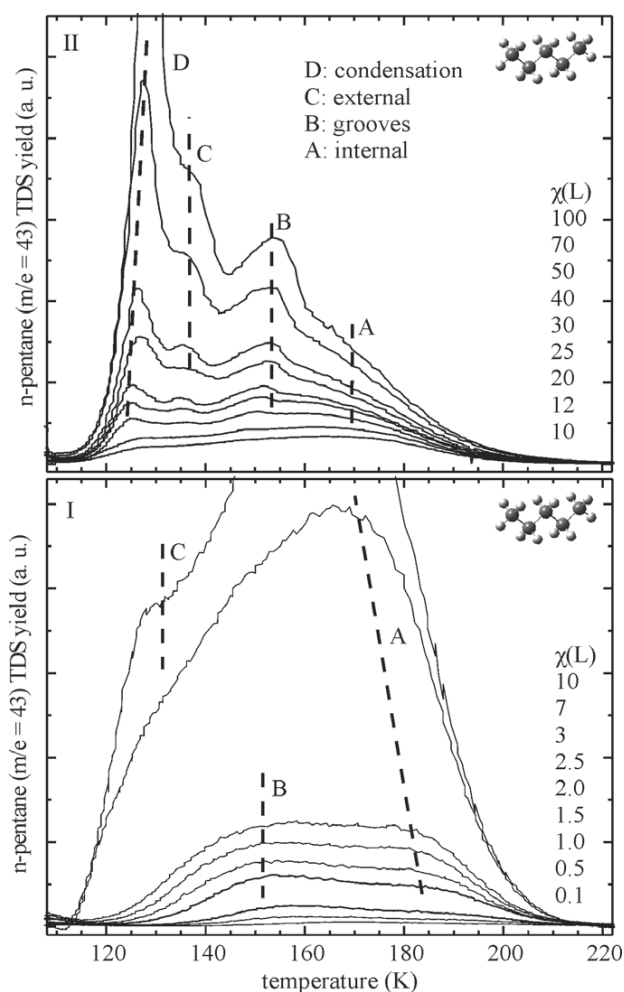


Fig. 1. *n*-Pentane TDS for low exposures (lower panel) and high exposures (upper panel).

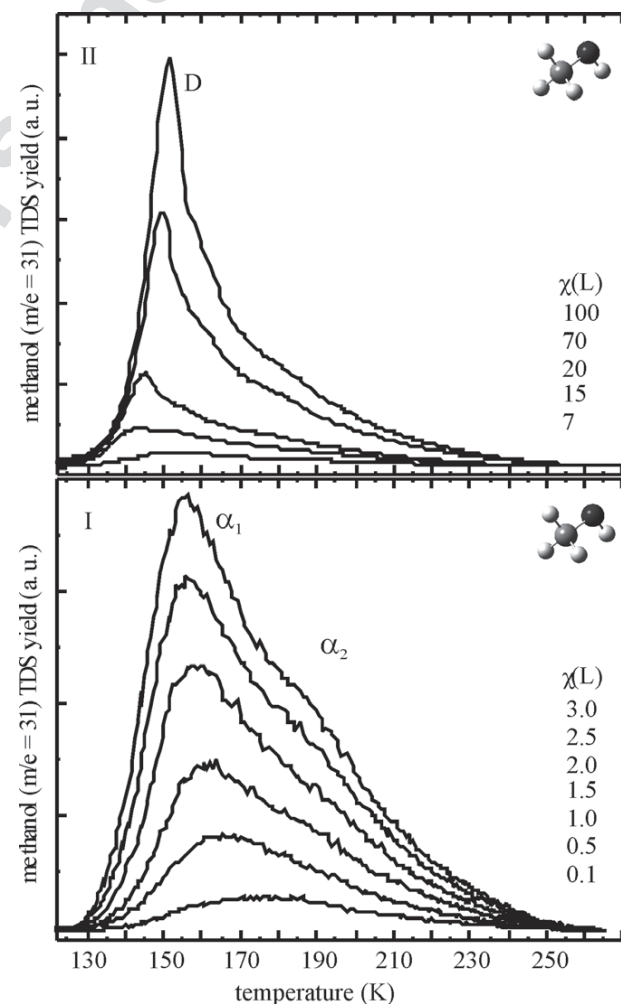


Fig. 2. Methanol TDS for low exposures (lower panel) and high exposures (upper panel).

open. Reference data collected for a bare silica support do not show any of those features [19]. The lining up of the low temperature edges of the curves reveals the D-peak as an adsorption site unspecific condensation structure.

Fig. 2 depicts TDS of MeOH adsorbed on the CNT monolayer. At large exposures the TDS curves are dominated by the desorption from a condensed layer (D-peak), as expected, since the low temperature edges line up indicating 0th-order kinetics (Fig. 2II). A leading edge analysis yields a binding energy of 28 kJ/mol, in agreement with Ref. [10], and a pre-exponential coefficient of $4 \times 10^{18}/s$ (cf., Refs. [20,21]). Unexpectedly, at small exposures only two structures are evident in MeOH TDS (α_1 and α_2 peak in Fig. 2I). Qualitatively similar results have been obtained with ethanol with TDS peaks shifted by ~ 20 K to larger temperatures [22]. Although the CNTs are open-ended, no distinct TDS features are present which have been reported for alkanes before [1,16] and were also present for the CNT sample studied here (Fig. 1).

Graphitic surfaces such as CNTs and HOPG are hydrophobic. Therefore the TDS data could be dominated by hydrogen bonding [10,23] within the adsorbed methanol

monolayer rather than by the methanol–CNT interactions. Thus, it appears plausible that no distinct features in MeOH/TDS have been observed which could easily be assigned to different adsorption sites on the CNTs.

However, one should consider possible side effects. An experimental difficulty in all studies of alcohol adsorption are water impurities which could lead to site blocking effects preventing, for example, that internal adsorption sites of the CNTs are occupied by MeOH. Therefore high purity methanol has been used (HPLC chromatography grade; water impurities below 0.05%). In addition, CaSO₄ (drierite) and an ice water trap have been used for some of the experiments in order to drop the possible water contamination level down. The TDS curves obtained with/without the cold trap were in agreement. Although a minor H₂O TDS feature has been seen (<10% of MeOH signal), it appears very unlikely that the results are obscured by water impurities. The TDS intensities detected at different settings of the mass spectrometer (e.g., $m/e = 31, 32$) agreed with the intensity ratios measured for gaseous methanol [24]. Additionally, decomposition fragments would cause side blocking effects in MeOH adsorption/desorption

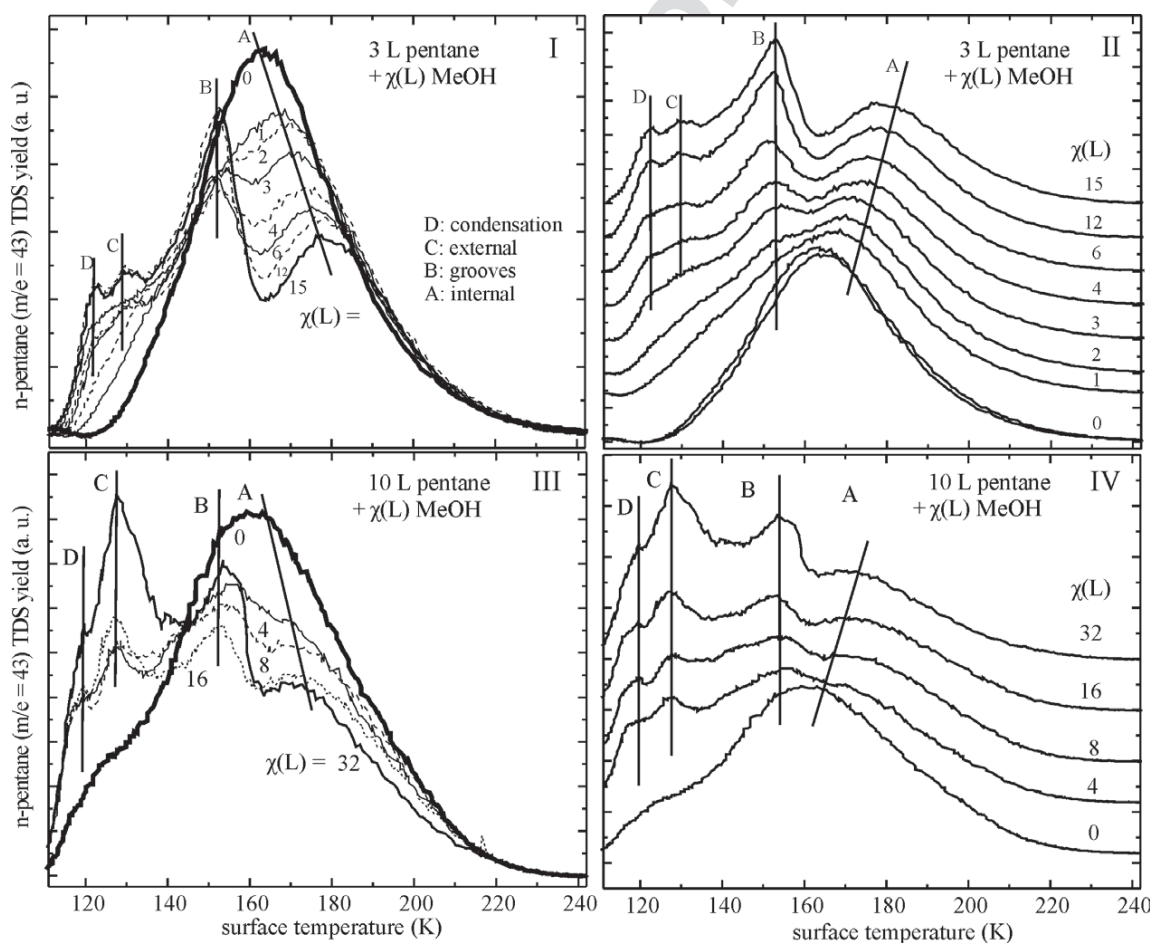


Fig. 3. *n*-Pentane/methanol co-adsorption experiments at small *n*-pentane exposure. The methanol pre-exposure has been varied; the *n*-pentane post-exposure has been kept constant, as indicated. The curves shown in the right column have been offset allowing for a better comparison of the curve shapes.

cycles which were not observed. Therefore, molecular adsorption can be concluded [10]. A Redhead analysis assuming a pre-exponential coefficient of $1 \times 10^{13}/s$ leads to binding energies of ~ 43 kJ/mol and ~ 51 kJ/mol corresponding to the α_1 and α_2 peaks, respectively. The maximum size of *n*-pentane amounts to 6.9 Å and is for methanol equal to 2.3 Å (according to a density functional based geometry optimization with GAUSSIAN). Thus, both molecules would be small enough to fit in the HiPco CNTs, which have an average tube diameter of 13.6 Å [25].

As a verification of this hypothesis, co-adsorption experiments were conducted in which first methanol and then *n*-pentane were exposed on the CNTs (see Fig. 3). Fig. 3 shows the *n*-pentane TDS for different methanol pre-exposures, as indicated, and constant *n*-pentane post-exposure – for 3 L (upper panel) and 10 L (lower panel) of *n*-pentane. In the right column of Fig. 3 the curves are offset to assist a comparison of the curve shapes whereas in the left column all curves are plotted over each other to allow for a simple intensity comparison.

The co-adsorption experiments show that initially the internal sites (A-sites) are preferentially occupied by methanol. For example, compare curves in Fig. 3I(III) obtained for 1 (4) L and 0 L of methanol. Increasing now the MeOH pre-exposure results in the sequential appearance of the groove (B-peak), external (C-peak), and condensation (D-peak) TDS features. The larger the MeOH pre-exposure the larger the intensities of the B, C, and D TDS peaks which is associated with a decrease in the A-peak intensity (see Fig. 3II/IV). The total area of the *n*-pentane TDS curves is conserved within an uncertainty smaller than 10% whereas the MeOH TDS signal increases with methanol exposure. The shift of the A-peak to larger desorption temperatures with decreasing occupation of internal sites with *n*-pentane is consistent with the effect of lateral interactions. Unfortunately, the TDS peaks overlap too strongly to clearly resolve related effect for the other adsorption sites. Thus, again it is evident that methanol and *n*-pentane compete about identical adsorption sites. Methanol replaces part of the initially on internal sites adsorbed *n*-pentane molecules leading to a decrease of the A-peak intensity in *n*-pentane TDS and in an increase in the B, C, and D TDS features. The binding energies of *n*-pentane and methanol do not differ enough to obtain more specific site blocking effects, i.e., the adsorbates form mixed layers. However, a partial replacement of internally adsorbed *n*-pentane to exterior sites on the CNTs is evident (Fig. 3). Using a combination of longer chain alkane/alcohol with a larger difference in binding energies would probably lead to more specific site blocking effects. However, in this case also larger flashing temperatures would be required which unfortunately lead to the destruction of the CNTs/silica sample. [4] Furthermore, MeOH is most important for applications.

In summary, evidence has been presented that methanol adsorbs on interior sites of the carbon nanotubes which

leads to an enhancement of the available total surface area of the catalyst. This will be important for applications such as direct liquid fuel cells. In addition and for the first time, kinetics parameters have been determined for the technologically relevant methanol adsorption on carbon nanotubes.

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