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and Implication for Hydrogen Storage**

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Interaction of D₂ with Ti-Adsorbed Polyaniline and Implication for Hydrogen StorageTae Seung Kim,[†] Kyung Jun Kim,[†] Sam K. Jo,[‡] and Jihwa Lee^{*,†}*School of Chemical and Biological Engineering, Seoul National University, Sillim San 56-1, Gwanak, Seoul 151-744, South Korea, and Department of Chemistry, Kyung Won University, Sungnam, Kyungki 461-701, South Korea**Received: April 16, 2008; Revised Manuscript Received: October 21, 2008*

Interaction of D₂ with Ti-adsorbed polyaniline (PANI) and TiO₂ at low Ti coverages has been investigated by temperature programmed desorption, Auger electron spectroscopy, and H₂–D₂ exchange in a high pressure cell. In contrast to recent DFT calculations (Lee et al. *Phys. Rev. Lett.* **2006**, 97, 56104–56107) that have shown a multiple number of molecular hydrogen chemisorption on Ti-decorated PANI, only 0.52 D₂ molecules per Ti *atomically* adsorb on Ti-deposited PANI at 87 K at a nominal Ti coverage of 2 ML. Broad TPD spectra of D₂, HD, and H₂ were observed, which showed a common peak at 250 K and another isotope-dependent peak at higher temperature. Ti deposited on TiO₂ forms clusters with a size distribution at 87 K, on which D₂ atomically adsorbs. As the Ti coverage increases, the D₂ desorption peak gradually shifts from 200 to 260 K and the number of D₂ molecules adsorbed per Ti also increases from 0.26 at 0.1 ML to 0.87 at 2 ML. We attribute this to the fact that D₂ adsorbs on larger clusters with a greater adsorption energy. TPD spectra of D₂ desorbing from Ti (2 ML)/PANI and Ti (1 ML)/TiO₂ look very similar to each other. This led us to conclude that Ti also adsorbs on PANI in clusters. We suggest that no molecular D₂ adsorption on Ti/PANI at 87 K is due to a reduced electron backdonation ability of Ti upon clustering. The small number of adsorbed D₂ per Ti on both substrates was ascribed to *irreversible* D₂ adsorption only on relatively large Ti clusters, while D₂ adsorbs *reversibly* on small clusters. This was indirectly confirmed by the observation that continuous H₂–D₂ isotope exchange occurs to produce HD on Ti/PANI as well as on Ti/TiO₂ at 106 K in a high pressure cell at 5.7 mTorr. Desorption mechanisms involving H atom abstraction from PANI by Ti clusters are proposed to account for the complex isotope-dependent TPD spectra. Implication of the present results for hydrogen storage based on Ti-dispersed polymers is briefly addressed.

1. Introduction

High prospects for hydrogen-fuel-cell-powered vehicles have stimulated much research on the hydrogen storage problem in recent years.¹ Among many different approaches, hydrogen storage based on reversible molecular hydrogen adsorption is the most attractive for its conceptual and operational simplicity. However, no suitable storage material which meets the economical capacity of ≥6.3 wt % at near ambient conditions has yet been demonstrated. The inherent difficulty lies in the fact that the physisorption energy of H₂ is too small due to its very small polarizability and zero dipole moment.

Very recently, it has been shown by density functional theory (DFT) calculations that hydrogen adsorbs molecularly onto early transition metals such as Sc, Ti, and V atomically dispersed on fullerenes,² carbon nanotubes,³ and various conducting polymers.⁴ For example, it is suggested that Ti atoms adsorb at two different sites on a polyaniline (PANI) chain, one above the benzene ring (out of plane) and the other between the N–H bond (in plane), as shown in Figure 1.⁴ While the first H₂ molecule adsorbs atomically, up to four H₂ molecules can bind to each in-plane Ti atom and three H₂ to each out-of-plane Ti atom with an average adsorption energy of 0.3–0.5 eV per H₂, respectively. A similar adsorption behavior has been suggested for metal–ethylene complexes.^{5,6}

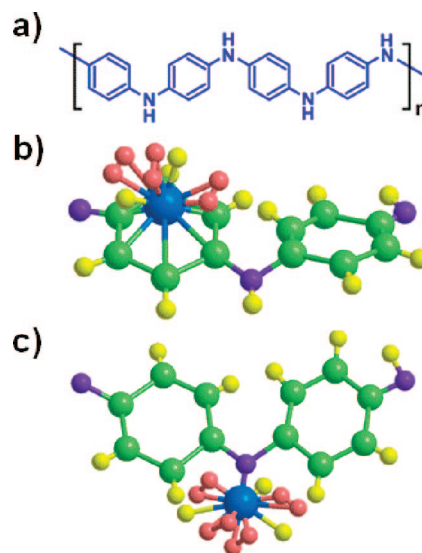


Figure 1. Structural formula of (a) leucoemeraldine–PANI; (b and c) the theoretically calculated bonding configurations of Ti-decorated PANI with adsorbed hydrogen (ref 4), where H (yellow), H₂ (brown), N (purple), C (green), and Ti (blue) are represented by colored spheres. Three and four H₂ molecules adsorb onto the Ti atoms coordinated with the phenyl ring (b) and inserted between the N–H bond (c), respectively.

Molecular H₂ binding to these transition metal atoms is known to occur via the so-called Kubas interaction,⁷ in which electrons are donated from the H₂ σ orbital to the empty metal d orbital

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and simultaneously backdonated from the filled metal d orbital to the unoccupied $H_2 \sigma^*$ orbital. The dihydrogen bonding to transition metal atoms is well-known for coordination compounds, and the H–H bond length widely varies depending on the degree of the electron backdonation to the $H_2 \sigma^*$ orbital.⁸ The unusually low vibrational energy of 398 meV observed for hydrogen adsorbed on a Ni (510) surface has also been attributed to molecular H_2 chemisorbed on the step sites by the Kubas interaction.⁹

The relatively large molecular adsorption energy of hydrogen on the transition-metal-decorated conducting polymers renders these materials ideal for reversible hydrogen storage with a high gravimetric density operating at moderate temperature and pressure conditions. Recent reports on an enhanced storage capacity of chemically reduced mesoporous and microporous Ti oxides by Hu et al.¹⁰ and of a low-coordinate Ti(III) complex grafted onto mesoporous silica by Hamaed et al.¹¹ have also been attributed to a similar H_2 interaction with coordinatively unsaturated Ti centers. At this point, it is quite desirable to experimentally verify molecular H_2 chemisorption on this kind of material and to define unforeseen practical problems in hydrogen storage application.

In this paper, we report results of experimental studies on the interaction of D_2 with Ti-adsorbed PANI by TPD, AES, and H_2 – D_2 isotope exchange at high pressure. In contrast to recent DFT calculations,⁴ no molecular chemisorption of D_2 was observed and only 0.52 D_2 molecules *atomically* adsorb per Ti on Ti-deposited PANI at 87 K. Upon heating, D atoms adsorbed on Ti react with H atoms of PANI to result in broad desorption spectra of D_2 , HD, and H_2 with a common peak at 250 K and another isotope-dependent higher temperature peak. We show that Ti adsorbs on PANI and TiO_2 in clusters and D_2 atomically adsorbs more strongly on a larger cluster. We further show that H_2 – D_2 isotope exchange to produce HD occurs on both samples via reversible hydrogen adsorption at 5.8 mTorr, from which we conclude that D_2 *reversibly* adsorbs on small clusters. Then, the discrepancy between the theory and experiment is discussed in terms of Ti clustering and size-dependent adsorption energies of atomically and molecularly adsorbed D_2 . Desorption mechanisms are also proposed to account for the complex isotope-dependent TPD spectra of D_2 -saturated Ti/PANI. Finally, implication of the present results for hydrogen storage is briefly mentioned.

2. Experimental Section

The experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 7×10^{-11} Torr pumped by a 540 L/s turbomolecular pump. It is equipped with a differentially pumped quadrupole mass spectrometer (QMS), an e-beam evaporator, instruments for Auger electron spectroscopy (AES), and a quartz crystal microbalance (QCM). The samples used are films (3000 Å) of leucoemeraldine base form of PANI (MW ~20000), the fully reduced form (Figure 1a), synthesized by a known procedure.^{12,13} The PANI was dissolved in tetrahydrofuran and spin-coated onto Si(100) wafers. After drying, the sample was mounted on a rotatable XYZ manipulator, and it could be cooled down to 87 K with liquid nitrogen or resistively heated to 1200 K. TiO_2 prepared by depositing Ti on a SiO_2/Si (100) wafer in an O_2 atmosphere and other organic substrate such as polyvinyl alcohol (PVA), polyethylene, and self-assembled monolayers of undecanethiol and mercapto-undecanol on Au(111) were also used as substrates.

A controlled amount of Ti was deposited *in situ* on the sample surface at 87 K by e-beam evaporation, and the coverage of Ti

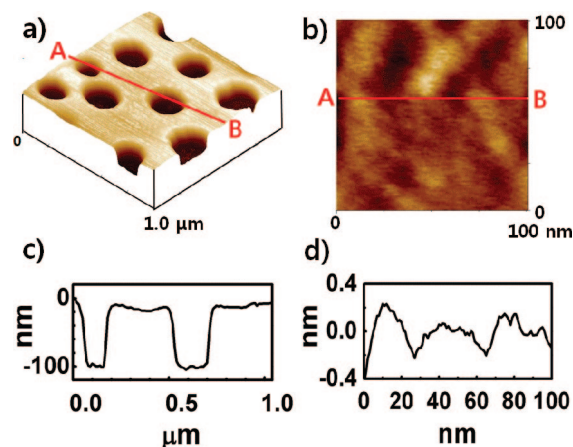


Figure 2. (a) AFM image of a PANI film (3000 Å) spin-coated on Si(100) wafer showing cylindrical pores; (b) phase contrast image of the PANI film of the smooth part of the surface. (c and d) Surface height profile along the line A–B in parts a and b, respectively.

was calibrated using a QCM. Unless specified otherwise, a *nominal* Ti coverage of 2 ML was typically employed. Here, we define the nominal 1 ML as the atom density (1.35×10^{15} atoms/cm²) of a hexagonally closed-packed Ti (0001) plane. According to the AFM image of the PANI film in Figure 2, the actual surface is at least twice that of a perfectly flat surface, and hence, *the actual Ti coverage on PANI is at most a half of the nominal one reported.*

TPD measurements were made by saturating the Ti/PANI samples at 87 K with D_2 using a gas doser. In TPD, molecules desorbing only from the front sample surface were detected by placing the sample very close to a protruding cylindrical aperture (5 mm diameter) in the wall of the differentially pumped QMS housing. A sample heating rate of 2 K/s was employed. Integrated TPD signals were calibrated against a separately measured, precisely known value for a 1 ML-saturated Si(100)- $2 \times 1:H$ surface. AES was performed with a 3 kV electron beam at a beam current of 1 μ A. Electron-beam-induced degradation of PANI sample was negligible, and surface charging was not observed at all.

H_2 – D_2 isotope exchange experiments were carried out in a small O-ring sealed high pressure cell (~200 mL volume) inside the UHV chamber. There is a micropinhole in the wall of the cell so that the partial pressures of the hydrogen isotope species in the cell leaking out into the UHV chamber can be monitored in real time with a QMS during the exchange reaction. The leak rates of hydrogen isotopes through the micropinhole were too small to cause an appreciable pressure decrease in the cell during a typical exchange reaction time of ~5 min. The data presented below were corrected for the mass-dependent effusion rates measured by filling the cell with a 1:1 H_2/D_2 gas mixture in the presence of a Ti-free PANI sample.

3. Results and Discussion

3.1. Surface Morphology of PANI. The AFM images of a typical PANI sample are shown in Figure 2. Interestingly, cylindrical pores of about 100 nm deep and 200 nm in diameter are randomly distributed on a relatively flat surface with a root-mean-square roughness of ~5 Å. The density of the pores counted from a scanning electron microscopy image of a much larger area is on average 8.5 pores/ μ m². If one assumes that the PANI chains are packed with the molecular planes parallel to the substrate, the maximum height variation corresponds to about two to three layers. If we neglect the height modulation,

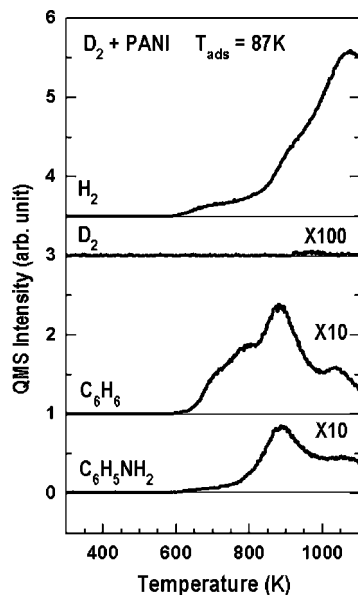


Figure 3. TPD spectra taken after exposing a pristine PANI at 87 K to 10^5 L of D₂ that show desorption of various thermal decomposition fragments above 600 K without any D₂ desorption.

the surface area is about 1.5 times larger than the nominal one because of the pores. The length l of the 1D height profile in Figure 2d can be calculated from the digital data to get the ratio $\alpha = l/d$, where d is the distance between the end points. The effective surface area is about α^2 times larger than the nominal one. The effective surface area estimated in this way is about 2.5 times that of the nominal one. Thus, the actual surface area of a typical PANI sample is about twice the nominal one.

3.2. TPD Spectra of D₂-Ti/PANI. Figure 3 shows the TPD spectra of various species desorbing from a pristine PANI after dosing the sample at 87 K with D₂ to saturation. No D₂ desorption is observed in the entire temperature range, and PANI starts to decompose above ~ 600 K to result in desorption of H₂ along with small amounts of C₆H₆ and C₆H₅NH₂. The result clearly shows that D₂ does not adsorb on PANI even at 87 K, which is in contrast to a recent report by Cho et al.^{14,15} that a HCl-treated PANI absorbs a large amount of H₂ (~ 6 wt %) at room temperature under 9.3 MPa. However, Panella et al.¹⁶ could not reproduce their results. H₂ interacts with an acid-doped PANI to induce a reversible change in the conductivity at room temperature, but a dedoped PANI shows no such a response¹⁷ in agreement with our result.

In contrast to Ti-free PANI, Ti-adsorbed PANI starts to decompose at ~ 250 K to give a broad H₂ desorption peak centered at ~ 370 K with a tail extending to higher temperatures (Figure 4a). H₂ is the only desorbing species below 600 K. *Ti-catalyzed H₂ desorption* is evident from the low desorption onset temperature of ~ 250 K. Ti presumably abstracts H atoms from the PANI chains, whereby recombinative desorption of H₂ occurs on the Ti atom(s) with a lower activation energy compared to that from Ti-free PANI.

D₂ adsorbs on Ti/PANI at 87 K to result in TPD spectra of D₂, HD, and H₂, shown in Figure 4b–d, in which Ti deposition was made under a direct D₂ flux on the sample surface in order to eliminate interference by H₂ adsorption from the background gas during Ti deposition. All of the molecular hydrogen isotopes start to desorb at a very low temperature of ~ 110 K, giving a common peak at ~ 250 K in addition to an isotope-dependent peak at high temperatures. Integrating the TPD signals, we estimate that 0.43 D₂, 0.18 HD, and 0.10 H₂ molecules per Ti

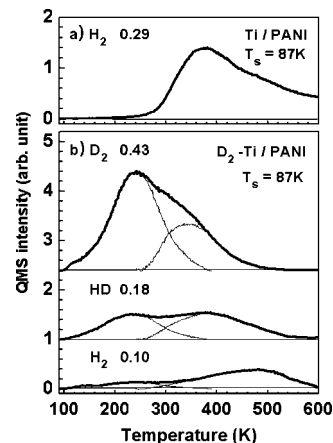


Figure 4. (a) Thermal decomposition spectra of Ti (2 ML)-deposited PANI showing H₂ desorption above ~ 250 K; (b) TPD spectra of D₂, HD, and H₂ desorbing from Ti (2 ML)/PANI saturated with D₂ at 87 K. A heating rate of 2 K/s was employed. The total number of hydrogen molecules desorbed per Ti is given for each spectrum. Resolving the spectra into two component peaks is described in the text.

desorb, which yields net D₂ adsorption of 0.52 D₂ per Ti. When the sample was exposed to D₂ for the second time after the first TPD run without further Ti deposition, D₂ did not adsorb at all. This indicates that Ti atoms have formed a stable compound with PANI during heating to 600 K to completely lose their adsorption capacity toward D₂.

The very broad spectra suggest that they consist of two overlapping peaks. Though somewhat arbitrary, we have resolved each spectrum into two components, a common peak at 250 K and the rest. These are designated as β_2 and β_1 peaks, respectively. We assign both β_1 and β_2 peaks to desorption of atomic hydrogen based on their large peak width¹⁸ and considerable isotope scrambling. The most significant TPD results are that (1) no molecular D₂ adsorption is observed on Ti/PANI and (2) only 0.52 D₂ molecules per Ti atomically adsorb at a Ti coverage of 2 ML. These are in sharp contrast to the DFT calculations by Lee et al.⁴ that predicted molecular adsorption of 3.5 H₂ in addition to atomic adsorption of one H₂ per Ti. This implies that Ti atoms do not bind to PANI as in Figure 1 but have some other bonding configurations under our experimental conditions.

3.3. Ti Clustering on PANI and TiO₂ Substrates. Recent investigations on the initial stage of interface formation in vapor deposition of Ti on various self-assembled monolayers^{19–22} and on nitrogen and halogen containing polymer surfaces²³ have shown that a large fraction of incident Ti atoms do not stick to these organic substrates at room temperature but form isolated clusters, indiscriminately reacting with the substrates. Isolated Ti clusters may also form on PANI, which may be the reason for the small number of D₂ molecules adsorbed per Ti. To check this possibility, we have performed TPD measurements with Ti atoms deposited on TiO₂/SiO₂ substrate at 87 K. D₂ desorption also starts at 110 K to give a peak at ~ 200 K at 0.1 ML, which gradually shifts with increasing Ti coverage to ~ 270 K at 2 ML (Figure 5). A higher temperature peak grows in at coverage ≥ 1 ML. According to DFT calculations by Kumar et al.,²⁴ the dissociative adsorption energy of H₂ monotonically increases with the number of Ti atoms in a cluster. Similar behavior has also been reported for Mg clusters.²⁵ Thus, the broad TPD spectra showing continuous peak shift in Figure 5 can be attributed to D₂ adsorption on Ti clusters formed on TiO₂/SiO₂ with a coverage-dependent size distribution.

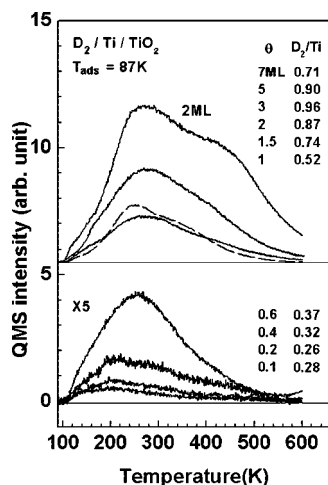


Figure 5. TPD spectra of D_2 desorbing from $Ti/TiO_2/SiO_2$ saturated with D_2 at 87 K for various Ti coverages. The number of the D_2 molecules adsorbed per Ti is given in the figure. The total D_2 ($D_2 + HD/2$) TPD spectrum taken with Ti (2 ML)/PANI is shown by the dashed curve for comparison.

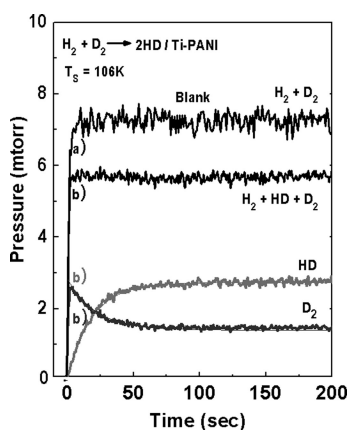


Figure 6. Time-dependent partial pressures of HD and D_2 in the reaction cell containing (a) Ti-free PANI and (b) Ti (2 ML)-deposited PANI samples, respectively, after the injection of 1.1×10^{-7} mol of a H_2 - D_2 (1:1) mixture gas into the cell. The partial pressure of H_2 could be measured accurately, but it is the same as that of D_2 .

Interestingly, the number of D_2 molecules adsorbed per Ti listed in Figure 5 is only 0.26 at 0.2 ML and almost linearly increases to 0.87 at 2 ML. Though not shown here, it reaches a maximum of 0.95 H_2/Ti at 3 ML and then decreases to 0.71 D_2/Ti at 7 ML. Clustering is not extensive at small coverage, and therefore, very small clusters are probably the dominant species. D_2 may adsorb on these small clusters reversibly even at 87 K because of its small adsorption energy; i.e., they all desorb immediately when D_2 dosing is stopped in UHV. Conversely, D_2 may adsorb irreversibly only on relatively large clusters.

Reversible hydrogen adsorption was indeed confirmed by the observation that continuous H_2 - D_2 isotope exchange occurs to produce HD on Ti/PANI (Figure 6) as well as on Ti/TiO_2 ²⁶ at 106 K when a 1:1 H_2 - D_2 mixture of 7.3 mTorr was introduced into a high pressure cell. Introduction of the gas causes the sample temperature to rise from 87 to 106 K due to gas conduction. If the TPD spectra in Figure 4b–d were obtained at 106 K instead of at 87 K, the number of D_2 molecules adsorbed per Ti would be smaller than 0.52 because hydrogen near the leading edge of the TPD spectra cannot remain adsorbed in UHV. Nevertheless, adsorption of 0.67 hydrogen molecules/

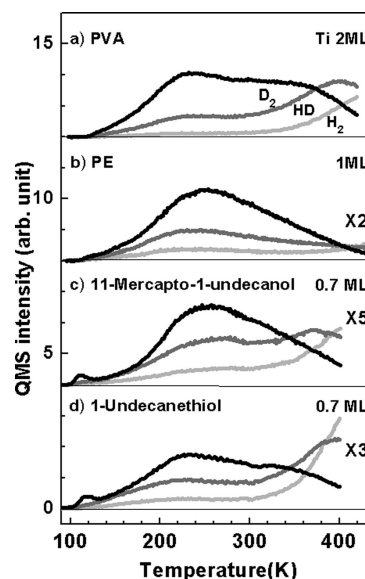


Figure 7. TPD spectra of molecular hydrogen isotopes desorbing from various Ti-deposited organic substrates saturated with D_2 at 87 K: (a) polyvinylalcohol (PVA); (b) polyethylene (PE); (c) self-assembled monolayer of 11-mercapto-1-undecanol on Au(111); (d) self-assembled monolayer of 1-undecanethiol on Au(111).

Ti is estimated from the difference in the final pressures in Figure 6. The significant amount of additional hydrogen adsorption is evidently due to reversible hydrogen adsorption at 5.7 mTorr. Thus, we attribute D_2 adsorbed per Ti much smaller than one on Ti/TiO_2 at ≤ 2 ML to reversible adsorption on small clusters. As the coverage increases, the average cluster size also increases and consequently more D_2 would adsorb irreversibly as observed. The decrease in D_2 adsorption beyond 3 ML can be attributed to the formation of 3D clusters which adsorb D_2 only on their surfaces.

We note that the total D_2 ($D_2 + HD/2$) TPD spectrum taken with Ti (2 ML)/PANI shown by the dashed curve in Figure 6 looks similar to that with Ti (1 ML)/ TiO_2 sharing common features: same onset temperature, similar peak temperature, ~ 0.5 D_2 molecules adsorbed per Ti, and H_2 - D_2 isotope exchange at high pressure. The similarity leads us to conclude that *Ti clusters also form on the PANI surface*. We also attribute the small number of D_2 adsorbed per Ti on Ti/PANI to reversible adsorption on small clusters. Similar spectra obtained at different nominal coverages could be due to different effective surface areas of the two substrates. TPD spectra (Figure 7) taken with samples such as PVA, PE, and SAMs on Au(111) suggest that Ti clustering and reaction with organic substrates below room temperature are general phenomena on organic substrates. All TPD spectra are qualitatively similar to those obtained with PANI, starting at ~ 110 K to give the β_2 peaks of D_2 and HD at 230–250 K. Ti clusters abstract H atoms even from PE which has only the $-CH_2-$ groups without any reactive functional group.

It has been shown previously by DFT calculations for Ti-decorated polyacetylene²⁷ and fullerene²⁸ that Ti clustering is energetically favored. Ti atom binds to PANI with a binding energy²⁹ comparable to that on polyacetylene (2.45 eV)²⁷ and fullerene (2.35 eV),²⁸ and hence, similar energetics is expected for Ti clustering on PANI. Ti clustering on these materials is driven by the large cohesive energy of Ti. Clustering reduces the number of molecularly adsorbed H_2 molecules as well as the adsorption energy of H_2 .^{27,28} A proper amount of electron backdonation to the D_2 σ^* orbital seems to be essential for

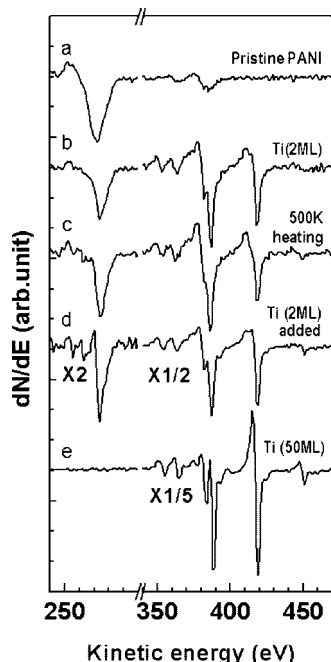


Figure 8. Auger electron spectra taken in sequence: (a) pristine PANI; (b) after depositing 2 ML of Ti at 87 K; (c) after D₂ saturation at 87 K followed by heating to 500 K; (d) after further depositing 2 ML of Ti at 87 K; (e) a reference spectrum for metallic Ti after depositing 50 ML of Ti.

molecular D₂ adsorption. When clustering occurs, much of their valence electrons are used to make strong Ti–Ti bonds and not many electrons are available for backdonation. This is believed to be the reason why we do not see in TPD a desorption peak of molecularly adsorbed D₂ on Ti/PANI at 87 K. One may argue that a majority of the reversibly adsorbed species in the exchange experiments could be molecular hydrogen weakly chemisorbed on small Ti clusters. We do not entirely rule out this possibility. If it is the case, one can roughly estimate the upper limit of the molecular adsorption energy as ~ 0.25 eV from the absence of a distinct desorption peak down to 90 K and the general relation³⁰ $E_{\text{des}} \sim 31 kT_p$ between the desorption activation energy (E_{des}) and the peak temperature (T_p) for first-order desorption.

3.4. Auger Electron Spectra of D₂–Ti/PANI. AE spectra (Figure 8) provide information on the bonding interactions of Ti with PANI. A pristine PANI shows a broad graphite-like C (KVV)³¹ peak of aromatic carbons at 271.9 eV and a N (KVV) peak at 384.0 eV. Upon adsorbing 2 ML of Ti at 87 K, the $L_{2,3}M_{2,3}M_{2,3}$ and $L_{2,3}M_{2,3}V$ peaks of Ti appear at 386.9 and 418.2 eV, respectively, and the C (KVV) peak is significantly attenuated by the overlying Ti atoms. However, the graphite-like carbon character is still maintained. No information is available from the N (KVV) peak because of its small peak intensity and interference by the close-lying Ti ($L_{2,3}M_{2,3}M_{2,3}$) peak. After a usual TPD run, the carbon peak now (Figure 9d) looks more or less like that of carbide-like carbon.³¹ Carbide formation is more clearly visible upon further depositing 2 ML of Ti at 87 K. The spectrum at the bottom is shown as a reference for metallic Ti obtained with 50 ML of Ti.

We note that for metallic Ti the peak-to-peak height of the $L_{2,3}M_{2,3}V$ peak is larger than that of the $L_{2,3}M_{2,3}M_{2,3}$ peak, whereas the opposite is true for Ti adsorbed on PANI. Similar observations have been made with titanium carbide³² and nitride.³³ Since the Ti ($L_{2,3}M_{2,3}V$) Auger transition involves one valence electron, the transition probability depends on the local

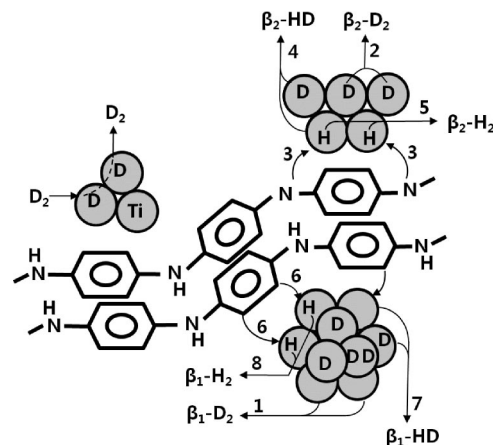


Figure 9. Schematic picture showing adsorption and desorption of hydrogen on Ti-deposited PANI. The numbers indicate elementary reactions leading to the desorption peaks of D₂, HD, and H₂ in the TPD spectra of Figure 4 (refer to the text).

valence electron density at a Ti atom and hence on the chemical environment of Ti. The smaller Ti ($L_{2,3}M_{2,3}V$) peak compared with the Ti ($L_{2,3}M_{2,3}M_{2,3}$) peak can be attributed to the fact that Ti clusters form polar bonds with PANI at 87 K to acquire a positive charge. Phenyl rings in contact with Ti clusters lose their H atoms during TPD, turning to TiC_x. No D₂ adsorption in the second D₂ dose is due to the carbide formation.

3.5. Adsorption and Desorption of Hydrogen on Ti/PANI.

On the basis of the TPD and AES results presented above, we now can draw a fairly consistent picture of the adsorption and desorption of hydrogen on Ti/PANI, as schematically depicted in Figure 9, where each number represents an elementary process described below. Ti adsorbs on PANI in clusters at 87 K with a certain size distribution, and the average cluster size increases with increasing Ti coverage. These clusters form polar bonds with carbon atoms without abstracting phenyl hydrogen. D₂ atomically adsorbs only on relatively large clusters. The β_1 (1) and β_2 (2) peaks of D₂ are evidently due to recombinative desorption of D atoms adsorbed on these clusters. The two peaks are associated with Ti clusters of different sizes coexisting on the surface. On the other hand, H atoms desorbing as HD and H₂ have to come from PANI because H₂ adsorption from the background was blocked by depositing Ti in a D₂ atmosphere. When properly scaled, the β_2 peaks of D₂ and HD exactly coincide with each other up to the peak temperature. This indicates that they desorb by the same mechanism. Namely, Ti clusters partially abstract H atoms from PANI which they are in contact with upon deposition at 87 K, and the abstracted H atom recombines with a D atom adsorbed on the cluster to give the β_2 -HD peak (4). As the bonding configurations of Ti in Figure 1 suggest, H atoms are probably abstracted from the more vulnerable –NH– moiety (3) rather than from the phenyl ring.

Large Ti clusters can abstract more than one H atom from the –NH– groups, and these H atoms recombine with one another to desorb as the β_2 -H₂ peak (5). However, the probability of H–D recombination is much greater compared to that of H–H recombination because the D atom is the majority species on a cluster at low temperature, and therefore, the intensity of the β_2 -H₂ peak is very small. Referring to the Ti-catalyzed PANI decomposition in Figure 4a, we attribute the β_1 peaks of HD and H₂ to desorption involving H atoms migrating from phenyl rings to Ti clusters (6) above ~ 250 K. These H atoms either recombine with a D atom or with another H atom to desorb as HD (7) and H₂ (8), respectively. When the sample temperature

reaches ~ 300 K, about one-third of the total adsorbed D atoms on large Ti clusters are still left. Thus, H atoms migrating to a Ti cluster will preferentially recombine with a D atom to desorb as β_1 -HD (7). On the other hand, at a later stage, little D atoms are left on the cluster and then the migrating H atoms will predominantly recombine with one another to desorb as β_1 -H₂ (8). The difference of ~ 100 K between the peak temperatures of the two β_1 peaks can be qualitatively explained.

3.6. Implication for Hydrogen Storage. In contrast to recent DFT calculations,⁴ no molecular D₂ adsorption was observed and only 0.52 D₂/Ti atomically adsorb on Ti-deposited PANI at 87 K. This implies that Ti atoms do not bind to PANI as theoretically predicted. This is also the case with other organic substrates. It seems that Ti-dispersed polymer is not a good medium for hydrogen storage. The main obstacle is Ti clustering favored by the large cohesive energy of Ti, which may be assisted by a poor energy transfer in the collision of incident Ti atom with polymer surfaces. Thus, Ti clustering is unavoidable in physical vapor deposition on organic substrates. Abstraction of H atoms from polymer chains by Ti below room temperature can also be a problem. The high reactivity of Ti is also associated with Ti clustering. In practical application, atomic dispersion of Ti in the bulk of polymer is needed, which is a challenging problem. However, the problems may be overcome by employing other clever Ti dispersion methods or by properly designing polymer structure so that strongly Ti-binding functional groups can be spatially separated. From this point of view, metal organic frames³⁴ can be a good candidate, though a high gravimetric storage density is difficult to achieve because of their large masses.

4. Summary and Conclusion

In contrast to recent DFT calculations, only 0.52 D₂ molecules per Ti atomically adsorb on Ti-deposited PANI at 87 K at a nominal Ti coverage of 2 ML. Broad TPD spectra of D₂, HD, and H₂ were observed, which showed a common peak at 250 K and another isotope-dependent peak at higher temperature. The TPD spectra of D₂ desorbing from Ti/TiO₂ show gradual peak shift from 200 to 260 K and an almost linear increase in the number of adsorbed D₂ molecules per Ti from 0.26 at 0.1 ML to 0.97 D₂/Ti at 3 ML. This was interpreted as the deposited Ti forms clusters of various sizes and the adsorption energy of D₂ increases with increasing cluster size. As a result, D₂ adsorbs irreversibly only on relatively large clusters while reversibly on small clusters. Ti also forms clusters on PANI and other organic substrates, resulting in TPD spectra qualitatively similar to that from Ti/TiO₂. Reversible adsorption was confirmed by the observation that continuous H₂-D₂ isotope exchange occurs on Ti/PANI and on Ti/TiO₂ in a high pressure cell at 7.3 mTorr and 0.15 more hydrogen molecules/Ti adsorb than that in TPD. Thus, we attribute the small number of atomically adsorbed D₂ molecules on Ti/PANI to weak reversible adsorption on small clusters.

Mechanisms of desorption from D₂-saturated Ti/PANI are proposed; Ti clusters formed upon deposition at 87 K abstract H atoms from the -NH- groups, and D₂ atomically adsorbs on the clusters. Upon heating, these D and H atoms recombine with one other to give desorption peaks of D₂, HD, and H₂ at 250 K. Above ~ 250 K, Ti clusters also abstract phenyl H atoms, which recombine with a D atom left on the cluster or with each other to give desorption peaks of HD and H₂, respectively, at

higher temperatures. Recombination of D atoms adsorbed on large clusters also gives a high temperature peak. Phenyl rings lose their H atoms during TPD, whereby carbon atoms convert to a carbide, losing their adsorption capacity toward D₂.

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