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Published on Web 05/28/2009

Desulfurization of Thiophene on Au/TiC(001): Au−C Interactions and Charge Polarization

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Abstract: Photoemission and first-principles DF calculations were used to study the interaction of thiophene with TiC(001) and Au/TiC(001) surfaces. The adsorption strength of thiophene on TiC(001) is weak, and the molecule desorbs at temperatures below 200 K. The molecule binds to Ti centers of TiC(001) through its sulfur atom with negligible structural perturbations. In spite of the very poor desulfurization performance of TiC(001) or Au(111), a Au/TiC(001) system displays a hydrodesulfurization activity higher than that of conventional Ni/MoS$_x$ catalysts. The Au↔TiC(001) interactions induce a polarization of electron density around Au which substantially increases the chemical reactivity of this metal. Au nanoparticles drastically increase the hydrodesulfurization activity of TiC(001) by enhancing the bonding energy of thiophene and by helping in the dissociation of H_2 to produce the hydrogen necessary for the hydrogenolysis of C−S bonds and the removal of sulfur. H_2 spontaneously dissociates on small two-dimensional clusters of gold in contact with TiC(001). On these systems, the adsorption energy of thiophene is 0.45−0.65 eV larger than that on TiC(001) or Au(111). Thiophene binds in a η^5 configuration with a large elongation (∼0.2 Å) of the C−S bonds.

1. Introduction

Recently, gold has become the subject of a lot of attention due to its unusual catalytic properties when dispersed on some oxide supports.[1−10] Bulk metallic gold is a very poor agent for the activation of molecules typically used in catalysis (H_2, O_2, CO, C_2H_4, etc.),[11,12] but atomic or molecular species bonded to low-index single crystal gold surfaces are chemically active.[13−15] Several models have been proposed for explaining the catalytic activity of gold/oxide surfaces: from special chemical properties resulting from the limited size of the active gold particles (usually less than 10 nm) to the effects of metal↔support interactions (i.e., charge transfer between the oxide and gold).[1−10] In principle, the active sites for the catalytic reactions could be located only on the supported Au particles or on the perimeter of the gold−oxide interface.[1,3,4,6] What happens when Au is deposited on a substrate which has physical and chemical properties different from those of an oxide? The carbides of the early transition metals exhibit, in many aspects, a chemical behavior similar to that of very expensive noble metals (Pt, Pd, Ru, or Rh).[16] Transition metal carbides exhibit broad and amazing physical and chemical properties.[16−18] Their properties may be viewed as resulting from a combination of those of covalent solids, ionic crystals, and transition metals.[16,18−20] In a recent study,[21] high-resolution photoemission, scanning tunneling microscopy (STM), and first-principles density-functional (DF) slab calculations were used to study the adsorption of gold on a TiC(001) surface. The Au↔TiC(001) interactions were much stronger than typical Au↔oxide interac-

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10.1021/ja901522a CCC: $40.75

tions. The photoemission and DF results point to the formation of Au−C bonds. In general, the bond between Au and the TiC(001) surface exhibits very little ionic character, but there is a substantial polarization of electrons around Au[21] which enhances the chemical activity of this metal.[21−23]

In this article, we investigate the bonding and hydrodesulfurization (HDS) of thiophene on Au/TiC(001) surfaces. C_4H_4S and its derivatives are common impurities in petroleum, and they must be removed in oil refineries through HDS processes.[24] The aromatic ring in thiophene makes its C−S bonds quite stable, and for this molecule the desulfurization reactions are much more difficult than those for other sulfur containing molecules such as thiols or SO_2.[25] Recent legislation has emphasized the need for reducing the sulfur content in oil-derived fuels, triggering an effort aimed at finding new and more efficient HDS catalysts.[26] Metal carbides have shown the potential to replace MoS_x-based catalysts in HDS processes.[16,18,25,26] The HDS catalytic activity of metal carbides can decrease due to the effects of sulfur poisoning.[26−28] To avoid deactivation, one must pay attention to the metal/carbon ratio in the carbide.[27] TiC(001) exhibits moderate bonding interactions with atomic sulfur.[29] We find that the Au/TiC(001) system is able to perform the hydrodesulfurization of thiophene, showing an activity higher than the activity of a conventional Ni/MoS_x catalyst. The polarization of Au on TiC(001) is essential for this process. The Au clusters substantially increase the hydrodesulfurization activity of TiC(001) by enhancing the bonding energy of thiophene and by helping in the dissociation of H_2 to produce the hydrogen necessary for the hydrogenolysis of C−S bonds and the removal of sulfur.

2. Experimental and Theoretical Methods

2.1. Experimental Studies. Photoemission studies for the adsorption of thiophene on TiC(001) and Au/TiC(001) were performed in a conventional ultrahigh-vacuum (UHV) chamber (base pressure ∼5×10^{-10} Torr) located at the U7A beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.[21,29] The chamber contains a hemispherical electron energy analyzer with multichannel detection, instrumentation for low-energy electron diffraction (LEED), a quadrupole mass spectrometer, and a dual anode Mg/Al Kα X-ray source. The Au 4f, S 2p, and Ti 2p spectra reported in section 3 were recorded using photon energies of 250, 380, and 550 eV, respectively. The overall instrumental resolution in these photoemission experiments was ∼0.3 eV. The binding energy scale in the photoemission spectra was calibrated by the position of the Fermi edge in the valence region. Additional experiments of X-ray photoelectron spectroscopy (XPS) were carried out using a UHV chamber (base pressure ∼1×10^{-10} Torr) that has capabilities for this technique plus low-energy electron diffraction (LEED), thermal desorption spectroscopy (TDS), and Auger electron spectroscopy (AES). This UHV chamber has attached a high-pressure cell or batch reactor[30] that was used to test the hydrodesulfurization activity (1 Torr of thiophene, 500 Torr of H_2, 600 K, 90 min reaction time) of a series of Au/TiC(001) surfaces. The amount of C_4 hydrocarbons formed during the HDS of thiophene was determined using a gas chromatograph with a flame ionization detector. In our studies, the catalyst sample was transferred between the reactor and vacuum chamber without exposure to air. Experiments were also performed at a UHV chamber located at the Tokyo Institute of Technology with capabilities for XPS, TDS, and scanning tunneling microscopy (STM).[21,22]

The TiC(001) single crystal was mounted and cleaned following the methodology described in refs 29 and 31. The cleaning procedure led to a clear 1 × 1 diffraction pattern in LEED and no surface impurities in photoemission or XPS. The crystal growers estimated a $TiC_{0.95-0.98}$ stoichiometry for the bulk of the sample, and after cleaning our quantitative XPS results showed surfaces with essentially a C/Ti ratio of 1.[29,31] Au was vapor deposited on TiC(001) at room temperature. The flux from the metal doser was calibrated by depositing Au on a Mo(100) crystal and taking thermal-desorption spectra of the admetal.[21,22] In the photoemission experiments, high-purity thiophene (Aldrich) was dosed to the TiC(001) and Au/TiC(001) surfaces at 100, 300, and 500 K.[32] Pressure increases measured with an ion gauge were used to control the doses of C_4H_4S. The relative coverages of sulfur species on the carbide surface were determined by measuring the area under the S 2p signal. For small amounts of adsorbed sulfur, these values were transformed into absolute coverages by using a p(2 × 2) to disorder overlayer transition seen in LEED for S/TiC(001).[29] The sulfur coverages are reported with respect to the number of Ti atoms in the TiC(001) surface.

2.2. Theoretical Studies. The density-functional (DF) calculations were performed with the VASP or $DMol^3$ codes, as detailed in refs 20, 21, and 33. In the past, we have found that DF calculations with VASP and $DMol^3$ give very similar results for adsorption geometries and the energetics of surface reactions on metal carbides.[20,21] Following a previous study,[21] VASP was used to investigate the nature of the Au↔TiC(001) interactions. This code uses a plane-wave basis set with a cutoff to the kinetic energy

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of 415 eV. The atomic cores are represented by the projected augmented plane-wave method of Blöchl. The VASP calculations were done with the PW91 form of the generalized gradient approximation for the exchange correlation functional.[20,21] To better understand the nature of the interactions of Au with TiC(001), the electronic structure has been analyzed through a topological analysis of the Electron Localization Function (ELF),[34] and charge distributions were estimated by the method of Bader.[35] To be able to directly compare with results reported in the literature,[21,22] the bonding of thiophene to Au clusters and Au/TiC(001) was examined with DMol^3 including all the electrons and relativistic effects.[33] Molecules, nanostructures, and extended surfaces were treated with the same level of accuracy. The DMol^3 calculations used the RPBE functional and numerical basis sets with comparable accuracy to a Gaussian 6-31G (d) basis set. Slabs of three or four atomic layers were utilized to model the TiC(001) substrate.[21,33] During the DF calculations the geometries of the first layers of the TiC and the Au adatoms were allowed to fully relax together with the adsorbed molecule. Using the final optimized geometries, the adsorption energies were calculated by means of the following equation:

$$E_{\text{ads}} = E_{\text{thiophene/surface}} - (E_{\text{thiophene}} + E_{\text{surface}}) \qquad (1)$$

where E_{surface} is the total energy of the relaxed surface, $E_{\text{thiophene}}$ is the energy of a isolated thiophene molecule in the vacuum, and $E_{\text{thiophene/surface}}$ is the energy of the system with adsorbed thiophene. A negative value of E_{ads} denotes an exothermic process.

3. Results and Discussion

3.1. Interaction of Thiophene with TiC(001): Photoemission and DF Studies. The top panel in Figure 1 shows S 2p spectra collected after adsorbing thiophene on TiC(001) at 100 K with subsequent heating to 180 and 200 K. The position of the S 2p features indicates that there is no C−S bond breaking.[28,32,36] The structure of thiophene remains intact, and the molecule desorbs from TiC(001) at temperatures between 150 and 200 K (bottom panel in Figure 1). TDS spectra acquired after dosing C_4H_4S to TiC(001) at 100 K showed a multilayer desorption peak at ∼135 K[32] and monolayer desorption from 150 to 190 K. From these experiments we estimate a thiophene adsorption energy of ~ -0.35 eV. For the TiC(001) surface used in the experiments of Figure 1, XPS spectra gave a C/Ti ratio of ∼1.[29,31] An enhancement in reactivity was found after bombarding TiC(001) with Ar^+ ions and producing surfaces with C/Ti ratios of 0.86−0.91. The adsorption on thiophene on these TiC_{1-x}(001) systems led to the appearance of S 2p features in the region 161−163 eV, which are characteristic of atomic S.[28,36] Thus, the presence of C vacancies is necessary for the full dissociation of the C−S bonds of thiophene on titanium carbide.

Thiophene can bind to a surface via its S lone pair (η^1 coordination mode) or through the aromatic ring of the molecule (η^5 coordination mode).[37] Figure 2 shows the calculated adsorption geometry for thiophene on TiC(001). Initially, thiophene was set with its molecular plane parallel to the surface. A geometry optimization yielded a bonding configuration in which the molecular plane is tilted with respect to the surface normal and the molecule is mainly interacting through the S atom with a Ti−S separation of 4.12 Å and a bonding energy of −0.1 eV. Clearly this result does not take into account the contribution from dispersion forces, but there is no doubt that the interaction is rather weak. Thus, the experimental and theoretical results show weak interactions between thiophene and stoichiometric TiC(001).

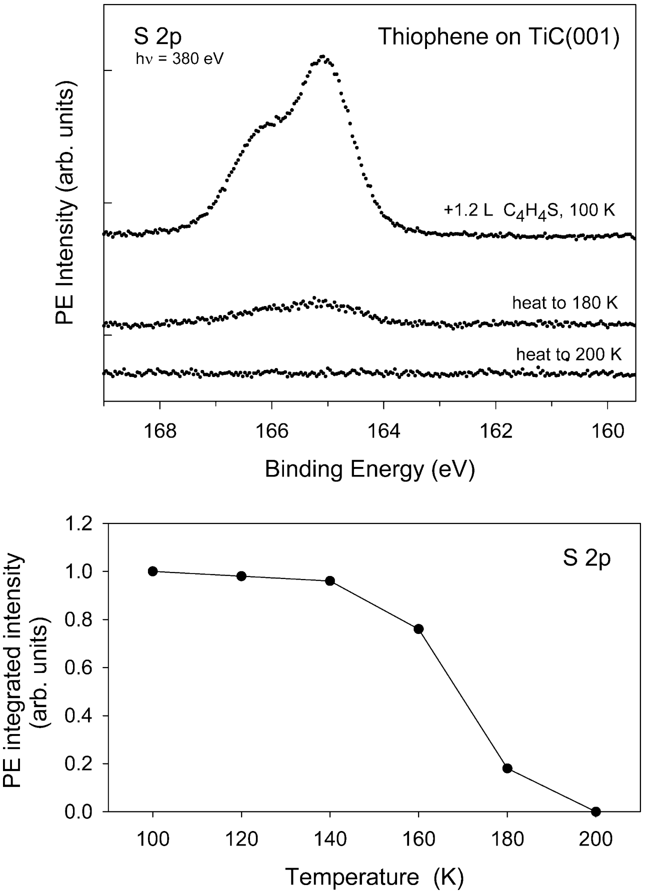

Figure 1. S 2p photoemission spectra acquired after dosing thiophene to TiC(001) at 100 K, followed by heating to the indicated temperatures. The electrons were excited using a photon energy of 380 eV. The bottom graph shows the variation of the S 2p signal for C_4H_4S/TiC(001) as a function of annealing temperature.

3.2. Adsorption and Desulfurization of Thiophene on Au/TiC(001): Photoemission and Catalytic Studies. As in the case of C_4H_4S/TiC(001), the bonding interactions of thiophene with Au(111) are weak and the molecule desorbs intact at temperatures below 250 K.[38] Figure 3 shows S 2p spectra recorded after dosing a small amount of thiophene at 100 K to a TiC(001) surface precovered with 0.2 ML of Au. The position of the S 2p features indicate that thiophene does not decompose on the Au/TiC(001) surface,[28,32,36] but the adsorption bond is substantially stronger than that on TiC(001). Molecules of thiophene (∼0.13 ML) are bonded to the Au/TiC(001) surface at 300 K, and complete desorption is only seen after heating to 450 K. After saturating the surface of Figure 3 with thiophene at 100 K (4 L exposure), a TDS spectrum showed multilayer desorption at ∼135 K[38] and monolayer desorption from 150 to 450 K. This indicates an increase of 0.45−0.65 eV in the adsorption energy of thiophene with respect to those on TiC(001) and Au(111). Figure 4 displays Au 3f core level spectra acquired before and after adsorbing thiophene on Au/TiC(001) at 100 K, with subsequent heating to 450 K. The adsorption of thiophene

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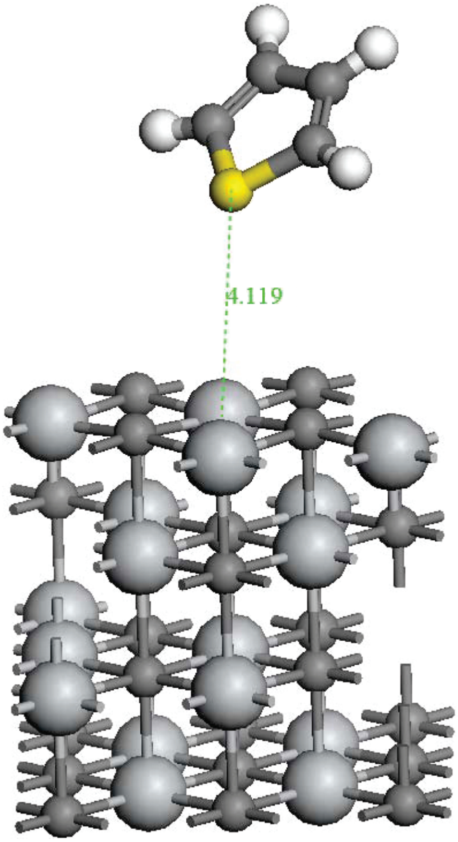

Figure 2. Calculated adsorption geometry for thiophene on TiC(001). The S end of thiophene is 4.119 Å above a Ti center of the TiC(001) surface. Color code: Ti is shown as large soft gray spheres, C as small dark gray spheres, H as small white spheres, and S as a small yellow sphere.

produces an attenuation and a negative binding-energy shift (~0.6 eV) in the Au 4f peaks. This indicates a direct Au↔C_4H_4S interaction, with thiophene covering the Au particles supported on TiC(001). Upon heating to 450 K, the thiophene desorbs and we essentially recover the initial intensity and binding energy of the Au 4f features.

Experiments similar to those in Figures 3 and 4 were done for a series of Au coverages on TiC(001). The strength of the Au↔C_4H_4S interactions depended strongly on the amount of gold deposited on the carbide substrate, top panel in Figure 5. At very small coverages of Au (~0.1 ML), thiophene remained on the surface up to 450 K. On the other hand, at Au coverages above 1.5 ML, the maximum thiophene desorption temperature was 280 K. Au grows on TiC(001) forming two- and three-dimensional particles.[21,22] STM images indicate that the height and size of the Au particles drastically change with coverage.[21,22] The bottom panels in Figure 5 show the distribution of heights observed with STM after depositing 0.1 and 0.5 ML of Au on TiC(001). For a coverage of 0.1 ML of Au, a large fraction of the Au particles exhibits a height of ~0.2 nm with respect to the carbide substrate. These small particles are two-dimensional (i.e., one single Au layer) and have a diameter below 0.6 nm.[22] When the Au coverage is increased to 0.5 ML, one sees a significant increase in the average height of the Au particles which are mainly three-dimensional. At Au coverages higher than 1 ML, one is dealing with three-dimensional Au particles which have sizes in the range 1.5 to 3 nm.[22] The trend in the top panel of Figure 5 reflects variations in the height and size of the Au particles: A large thiophene bonding energy is seen on small two-dimensional Au particles. This will be corroborated by the DF calculations discussed in section 3.3.

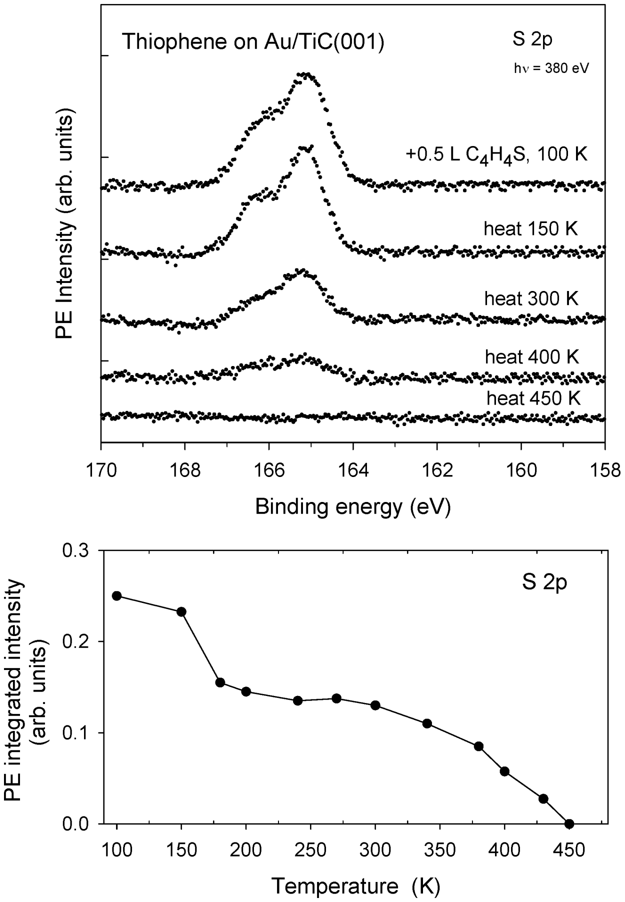

Figure 3. S 2p photoemission spectra ($h\nu = 380$ eV) acquired after dosing thiophene at 100 K to a TiC(001) surface precovered with 0.2 monolayers of Au. In subsequent steps, the sample was heated to the indicated temperatures. The bottom graph shows the variation of the S 2p signal for C_4H_4S/Au/TiC(001) as a function of annealing temperature.

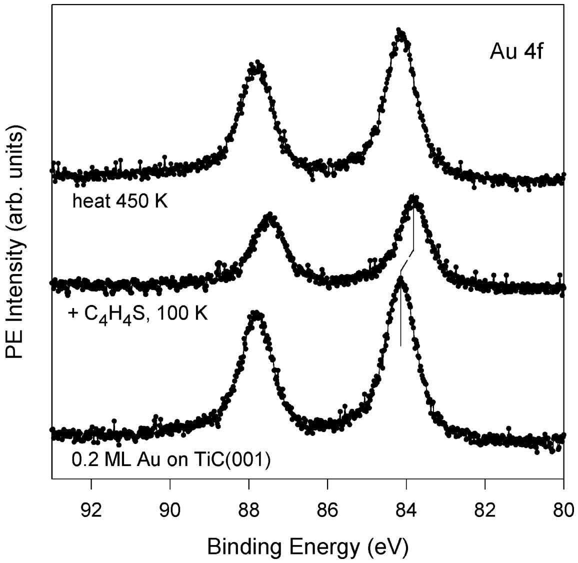

Figure 4. Au 4f photoemission spectra ($h\nu = 250$ eV) acquired before and after dosing thiophene at 100 K to a TiC(001) surface precovered with 0.2 monolayers of Au. In subsequent steps, the sample was heated to 450 K.

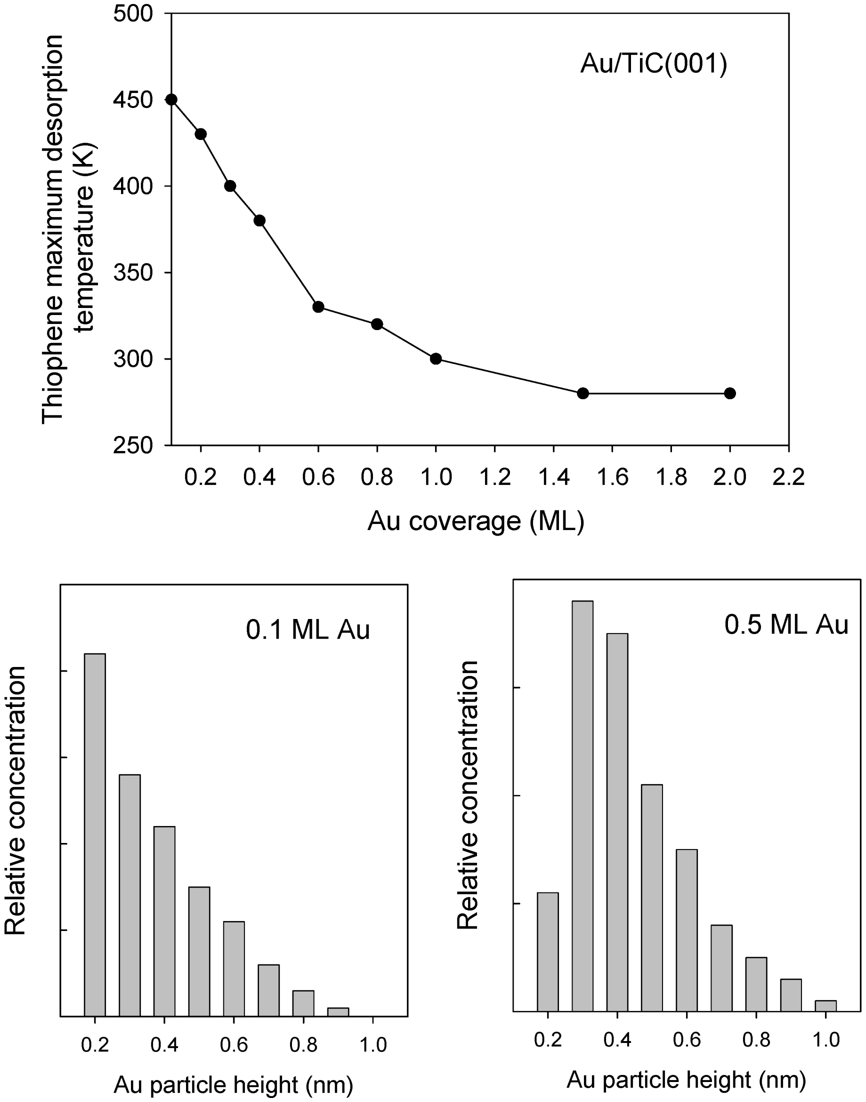

Figure 5. Top: Maximum thiophene desorption temperature from Au/TiC(001) as a function of gold coverage. The data were acquired in experiments similar to those shown in Figure 3. Bottom: Distribution of Au particle heights seen in STM images for 0.1 and 0.5 ML of gold on TiC(001). Au was deposited at 300 K, and the Au/TiC(001) surfaces were annealed to 550 K before the STM images were taken.

In the UHV experiments with the Au/TiC(001) surfaces we did not detect the cleavage of C−S bonds when thiophene was dosed at temperatures between 100 and 500 K. After exposing Au/TiC(001) surfaces to 1 Torr of thiophene at 300−500 K in a batch reactor for 5−10 min, we detected in the S 2p region small features at binding energies of 163−165 eV that could be attributed to a C_xH_yS species in which one of the C−S bonds in thiophene has been broken.[36] In HDS processes, H adatoms present in the surface of the catalyst can help in the cleavage of the C−S bonds of thiophene.[26,39,40] Gold nanoparticles are able to dissociate the H_2 molecule.[41,42] The top panel in Figure 6 shows S 2p XPS spectra recorded after exposing TiC(001) and a surface with 0.2 ML of Au to a mixture of thiophene (1 Torr) and H_2 (500 Torr) for 5 min at 300 K. In the case of TiC(001), no S 2p signal is observed for intact C_4H_4S, C_xH_yS species, or atomic S. The Au/TiC(001) system exhibits broad features which can be attributed to C_xH_yS species and atomic S.[29,36] Thus, the supported Au nanoparticles dramatically enhance the HDS activity of TiC(001). We were able to remove the C_xH_yS species and atomic S present on Au/TiC(001) by reaction with H_2 at 600 K (bottom panel in Figure 6). This was possible because neither Au nor TiC(001) bond sulfur very strongly.[27,29,43]

Following the results in Figure 6, we decided to test the catalytic activities of the Au/TiC(001) surfaces for the HDS of thiophene at 600 K. The catalysts were set in a batch reactor (1 Torr of thiophene, 500 Torr of H_2, 90 min reaction time), and the total amount of C_4 hydrocarbons formed was determined using gas chromatography. Under the reaction conditions investigated in this study, TiC(001) displayed negligible catalytic

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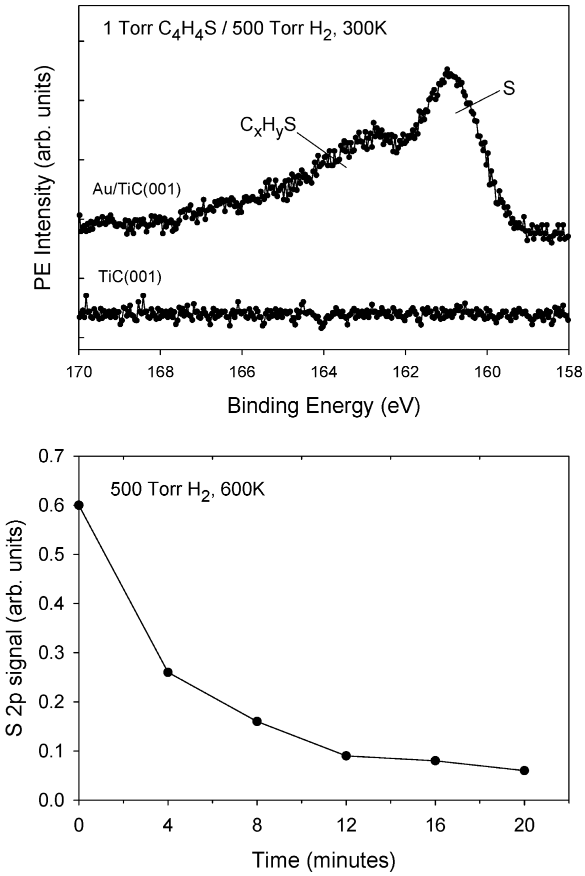

Figure 6. Top: S 2p XPS spectra recorded after exposing TiC(001) and a surface with 0.2 ML of Au to a mixture of thiophene (1 Torr) and H_2 (500 Torr) for 5 min at 300 K. Bottom: Hydrogenation of S adatoms and C_xH_yS fragments produced by the decomposition of thiophene on Au/TiC(001); see top panel. The sample was exposed to 500 Torr of H_2 at 600 K. The removal of sulfur was followed by measuring the changes in the total area of the S 2p XPS signal as a function of reaction time.

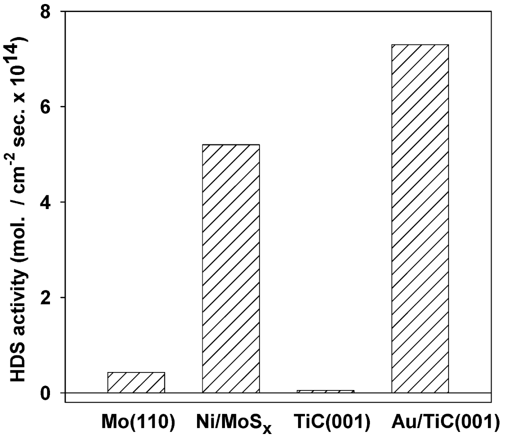

Figure 7. Thiophene HDS activities for Mo(110), a Ni/MoS_x catalyst,[32] TiC(001), and a Au/TiC(001) catalyst with 0.2 ML of Au. In the *y*-axis the total amount of C_4 hydrocarbons formed during the HDS of thiophene is plotted (1 Torr of thiophene, 500 Torr of H_2, 600 K, 90 min reaction time). The number of C_4 hydrocarbon molecules produced was normalized by the reaction time and the exposed surface area of each sample.

activity. On the other hand, Au/TiC(001) surfaces with Au coverages of 0.1−0.3 ML were very good HDS catalysts. Figure 7 compares the thiophene HDS activities measured for Mo(110),[36] a conventional Ni/MoS_x catalyst,[32] TiC(001), and a Au/TiC(001) catalyst with 0.2 ML of Au. The HDS activity found for Mo(110) is comparable to that seen in a previous study.[44] Similar HDS activities were observed for Mo(111) and Mo(100) surfaces.[44] The Mo surfaces are not good HDS catalysts because they interact too strongly with the sulfur produced after the cleavage of the C−S bonds in thiophene.[25,27,36] The conventional Ni/MoS_x catalyst has a much better performance and binds thiophene well[32] without being deactivated by the S atoms produced in the HDS process. Many industrial HDS catalysts contain a mixture of molybdenum sulfide promoted with Ni on a γ-alumina support.[39] In spite of the very poor desulfurization performance of Au(111) or TiC(001), a Au/TiC system displays an HDS activity higher than that of Ni/MoS_x. The DF calculations described in the next section show that small Au clusters drastically enhance the HDS activity of TiC(001) by increasing the bonding energy of thiophene and by helping in the dissociation of H_2 to produce the hydrogen necessary for the hydrogenolysis of C−S bonds and the removal of sulfur.

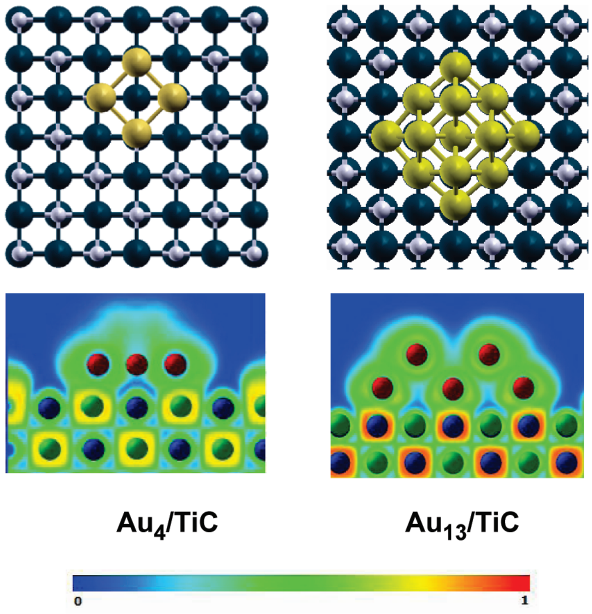

Figure 8. Top: Calculated adsorption geometries for Au_4 and Au_{13} on TiC(001). The Au_{13} cluster consists of nine atoms in its first layer, in contact with the carbide substrate, and four atoms in its second layer. Blue spheres denote Ti atoms, while white spheres represent C atoms. Gold is shown as dark yellow spheres. Bottom: ELF maps for Au_4 and Au_{13} on TiC (001). On the right side is shown a cut along the diagonal of the Au_{13} cluster in a plane which contains five gold atoms. The probability of finding the electron varies from 0 (blue color) to 1 (red color).

3.3. Interaction of Thiophene and H_2 with Au/TiC(001): DF Studies. Previous photoemission and DF results point to the formation of Au−C bonds in the Au/TiC(001) systems.[21] The top part of Figure 8 displays the calculated adsorption geometries for Au_4 and Au_{13} on TiC(001). Au_4 and Au_{13} are models for the two- and three-dimensional clusters of Au seen in STM images for Au/TiC(001). A Bader analysis of the electron density[35] showed a very small net charge transfer from the surface to the gold clusters (Q_{Au} < 0.2e). Figure 8 displays electron-polarization function (ELF)[34] plots for Au_4 and Au_{13} on TiC(001). In the case of Au_4/TiC(001), there is a substantial concentration of electrons in the region outside the Au_4 unit. A similar phenomenon was observed for Au, Au_2, and other small

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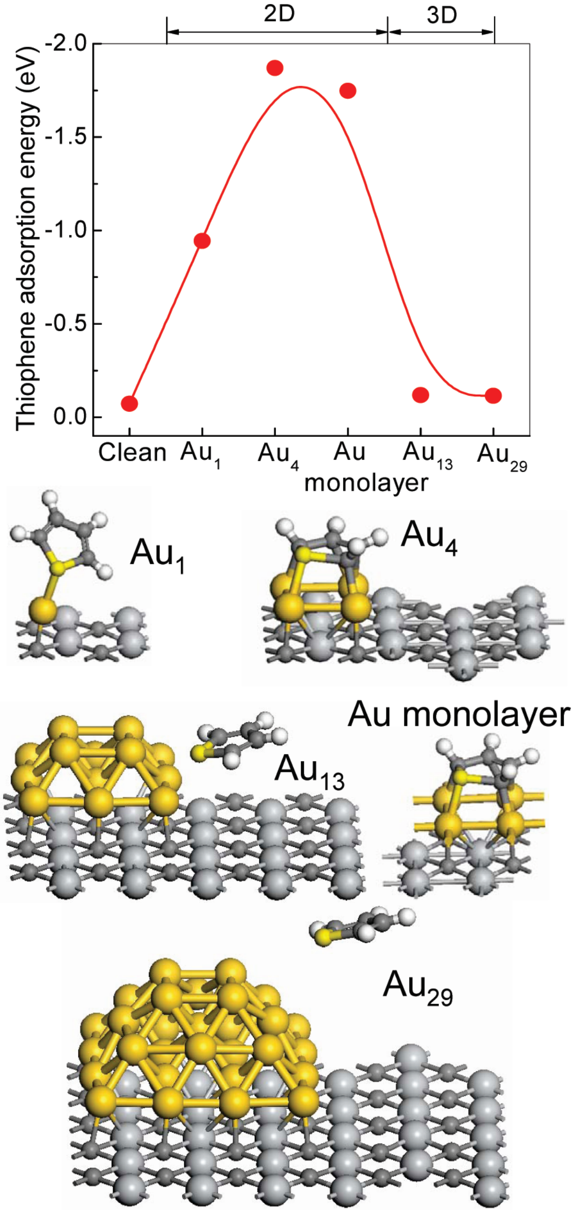

Figure 9. Top: Calculated adsorption energy for thiophene on TiC(001) and Au/TiC(001) systems containing isolated Au atoms, Au_4, Au_{13}, or Au_{29} clusters, and an ideally flat Au monolayer. The Au systems are separated in 2D and 3D overlayers. Bottom: Different adsorption geometries for thiophene. Color code: Ti is shown as large soft gray spheres, C as small dark gray spheres, Au as large yellow spheres, H as small white spheres, and S as a small yellow sphere.

clusters containing one layer of gold in contact with the carbide substrate.[21] In the Au_{13}/TiC(001) system, the Au cluster has two layers, and for the second layer the polarization of electrons is not as pronounced as seen in the case of Au_4/TiC(001). In fact, the polarization is yet only slightly noticeable in the first layer. The charge polarization induced by the carbide substrate leads to big differences between the chemical reactivity of two-dimensional (2D, i.e. single layer) and three-dimensional (3D) gold clusters.

Figure 9 shows the calculated adsorption energy for thiophene on Au, Au_4, an ideally flat Au monolayer, Au_{13}, and Au_{29} supported on TiC(001). The Au systems are separated in 2D and 3D overlayers. The calculated bonding energy between a single Au atom in gas phase and thiophene was −0.2 eV. On Au_1/TiC(001) the thiophene bonding configuration (η^1-S) is similar to that found for C_4H_4S-Au or on clean TiC(001) (see Figure 2), but there is an increase of ~0.8 eV in the bonding energy of the molecule. Thus, the electronic perturbations induced by TiC(001) on Au significantly enhance the $C_4H_4S \leftrightarrow Au$ bonding interactions. In the case of unsupported $C_4H_4S-Au_4$ the bonding energy of thiophene was ~ -1 eV and the molecule was attached to the metal cluster in an η^5 conformation. A similar bonding conformation was found on Au_4/TiC(001) (see bottom of Figure 9) with the bonding energy of thiophene increasing to ~ -2 eV. The electronic perturbations in gold also led to strong bonding interactions between thiophene and an ideally flat Au monolayer supported on TiC(001). In contrast, the Au atoms in the second layer of a supported Au_{13} cluster, or in the third layer of a supported Au_{29} cluster, exhibited weak bonding interactions with thiophene. The polarization of electrons around gold is essential for seeing strong adsorption interactions with thiophene. Therefore, the trend in the top panel of Figure 5 probably reflects a reduction in the number of Au atoms which are exposed to thiophene *and* directly in contact with the carbide substrate. A low coordination number of the Au sites is not sufficient for obtaining strong $Au \leftrightarrow C_4H_4S$ interactions.

In Figure 9, one can see a large distortion in the geometry of thiophene after adsorbing the molecule on Au_4/TiC(001) or Au(monolayer)/TiC(001). In gas phase, the calculated C−S bond distances in thiophene were 1.746 Å. Upon adsorption on Au_4/TiC(001), the C−S bond distances increased to an average value of ~1.93 Å. The LUMO of thiophene, the $3b_1$ orbital, is C−S antibonding.[37,45] The polarization of electrons seen in Figure 8 for Au_4/TiC(001) facilitates a transfer of charge from gold to the LUMO of thiophene which induces a quite large elongation (~0.2 Å) in the C−S bonds. Although the C−S bonds of thiophene are significantly weakened on Au_4/TiC(001) or Au(monolayer)/TiC(001), they do not dissociate spontaneously. The desulfurization of thiophene probably occurs through hydrogenolysis reactions.[26,39,40]

$$C_4H_4S(ads) + nH(ads) \rightarrow C_4H_{3+n}SH(ads) \qquad (2)$$

$$C_4H_{3+n}SH(ads) + mH(ads) \rightarrow C_4H_{2+n+m}(gas) + H_2S(gas) \qquad (3)$$

The dissociation of H_2 on TiC(001) is a slightly exothermic process ($\Delta E \approx -0.15$ eV) with an activation barrier close to 0.7 eV.[46] In contrast, the dissociation of H_2 on Au_4/TiC(001) was highly exothermic ($\Delta E \approx -1.8$ eV). We did not observe a stable adsorption minimum for H_2 on Au_4/TiC(001), and the molecule spontaneously dissociated to yield the system shown in Figure 10. A decrease in the reactivity for H_2 dissociation was seen when the size of the Au cluster increased, but a large Au_{29} particle was still able to dissociate H_2.[41] Furthermore, it has been shown that the necessary condition for H_2 dissociation is the presence of low coordinated sites, and these are present even for large Au nanoparticles.[42] Thus, in this respect, it is not surprising that a hydrogenolysis of the C−S bonds in thiophene occurs on a Au/TiC(001) surface, as seen in the experiments (top panel in Figure 6).

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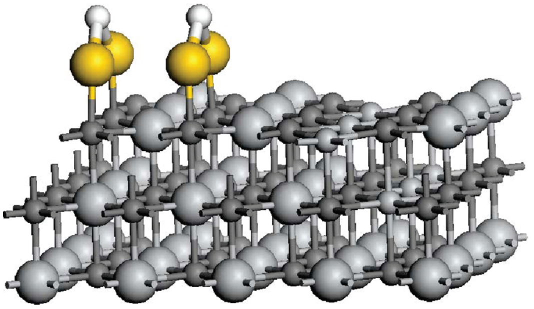

Figure 10. Adsorption geometry found after the spontaneous dissociation of H_2 on Au_4/TiC(001). Color code: Ti is shown as large soft gray spheres, C as small dark gray spheres, H as small white spheres, and Au as large yellow spheres.

The current commercial HDS catalysts cannot provide fuels with the low content of sulfur required by new environmental regulations.[24a,26,39] One option is to improve the performance of traditional molybdenum sulfide based HDS catalysts.[47] Another option involves the use of metal carbides or phosphides as HDS catalysts.[16,18,26,28] It has been established that β-Mo_2C and other metal carbides are very active for the cleavage of C−S bonds,[25,36,48] but their HDS activity decreases with time due to the formation of a chemisorbed layer of sulfur.[18,26,27,49] To avoid deactivation, one must pay attention to the metal/carbon ratio in the carbide.[27] TiC(001) exhibits moderate bonding interactions with sulfur[27,29] but interacts poorly with thiophene or H_2. After adding Au to TiC(001), one obtains a highly active HDS catalyst by obeying Sabatier's principle: good bonding with the reactants and moderate bonding with the products.

The enhancement seen here for the chemical activity of Au after depositing this noble metal on TiC(001) is more pronounced than that observed upon deposition on surfaces of oxides.[1−10] For Au on TiO_2(110), MgO(001), or ZnO(000$\bar{1}$), we did not find the large changes seen here for the bonding (Figure 5) and desulfurization (Figure 7) of thiophene. Even in the case of SO_2, a more reactive molecule than thiophene,[25] Au/MgO(001) surfaces are not able to dissociate the S−O bonds[50] while dissociation occurs on Au/TiC(001) at 100 K.[22] The Au↔C interactions induce a polarization of electron density around gold, and the bonding energy of Au on TiC(001) is 3−4 times larger than that on MgO(001) or TiO_2(110).[6,8a,51,52] Thus, the metal carbide is a better support for enhancing the chemical activity of gold nanoparticles than metal oxides. In addition, the C sites of TiC(001) are not simple spectators and can help with the bonding of intermediates generated in HDS reactions.[25,29]

4. Summary and Conclusions

Photoemission and first-principles DF calculations were used to study the interaction of thiophene with TiC(001) and Au/TiC(001) surfaces. The adsorption bond of thiophene on TiC(001) is weak, and the molecule desorbs at temperatures below 200 K. The molecule binds to Ti centers of TiC(001) through its S atom with negligible structural perturbations. In spite of the very poor desulfurization performance of TiC(001) or Au(111), a Au/TiC(001) system displays an HDS activity higher than that of conventional Ni/MoS_x catalysts. Au nanoparticles drastically increase the hydrodesulfurization activity of TiC(001) by enhancing the bonding energy of thiophene and by helping in the dissociation of H_2 to produce the hydrogen necessary for the hydrogenolysis of C−S bonds and the removal of sulfur. H_2 spontaneously dissociates on small two-dimensional clusters of gold in contact with TiC(001). On these systems, the adsorption energy of thiophene is 0.45−0.65 eV larger than that on TiC(001) or Au(111). Thiophene binds in an η^5 configuration with extensive elongation (∼0.2 Å) of the C−S bonds. These phenomena are a consequence of the large electronic perturbations induced on Au by the Au↔TiC(001) interactions.

Acknowledgment. The authors are grateful to B. Roldán-Cuenya (University of Central Florida) and J. Gomes (Universidade do Porto) for thought-provoking discussions about the properties of Au/TiC. Many thanks to T. Jirsak (BNL) for his help with the operation of the U7A beamline and the photoemission experiments at the NSLS. The research carried out at BNL was supported by the U.S. Department of Energy, Chemical Sciences Division. J.A.R. acknowledges the support of the *Generalitat de Catalunya* in a visit to the Universitat de Barcelona. F.V. thanks the Spanish Ministry of Education and Science and Universitat de Barcelona for supporting his predoctoral research. K.N. is grateful to the Nippon Foundation for Materials Science for grants that made possible part of this work. and F.I. acknowledges financial support from Spanish MICINN Grant FIS2008-02238/FIS. Computational time at the Center for Functional Nanomaterials at BNL and the *Marenostrum* supercomputer of the Barcelona Supercomputing Center is gratefully acknowledged.

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