

The Ti_8C_{12} Metcar: A New Model Catalyst for Hydrodesulfurization

Ping Liu, José A. Rodriguez,* and James T. Muckerman*

Department of Chemistry, Brookhaven National Laboratory, Bldg. 555, Upton, New York 11973

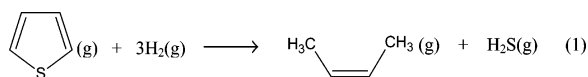
Received: October 5, 2004; In Final Form: October 26, 2004

Elementary reaction steps and barriers for thiophene hydrodesulfurization (HDS) on a Ti_8C_{12} nanoparticle were investigated using density functional theory. It is found that despite its high carbon concentration Ti_8C_{12} displays a superior catalytic potential for hydrodesulfurization. Compared to the industrial catalysts, the hydrogen dissociation and C–S bond cleavage on Ti_8C_{12} are more facile, and the removal of sulfur is energetically comparable. Our results also show that the catalytic activity of Ti_8C_{12} can be associated with its unique structure that is quite different from that of bulk metal carbides.

I. Introduction

A challenge of modern science is to characterize and understand the chemical behavior of metal compound nanoparticles. We are interested in the chemical properties of metallo-carbohedrene (metcar) species, an important new class of molecular clusters or nanoparticles.^{1,2} Since their discovery in the early 1990s, they have become one of the highlights in nanoscience.^{1–6} Bulk metal carbides have been found to display a superior ability to catalyze many chemical reactions,⁷ and the metcar nanoparticles, with their uniform size and fully characterized active sites, might be good model catalysts. Our calculations have shown that Ti_8C_{12} displays a reasonably high activity and stability in both gas phase^{8,9} and the metal-oxide supported forms ($\text{Ti}_8\text{C}_{12}/\text{MgO}(100)$).¹⁰

In the present letter we employ density functional theory (DFT) to investigate the catalytic potential of the Ti_8C_{12} metcar toward thiophene hydrodesulfurization (HDS), one of the typical HDS reactions in which sulfur is removed from crude oil.⁸ This is a very demanding process⁹ and there is a continuous search for catalysts that will replace the NiMoS and CoMoS catalysts used in industry.^{7a,12,13} The overall HDS reaction corresponds to a conversion of thiophene to *cis*-2-butene and hydrogen disulfide (eq 1).



Thiophene HDS is exothermic at room temperature (−1.48 eV). Thus, the conversion is merely inhibited by kinetics. Here, an HDS mechanism consisting of a sequence of elementary steps and their associated barriers for a complete catalytic cycle is determined using DFT. Our results show that Ti_8C_{12} propels thiophene HDS better than the commercial catalyst in terms of H_2 dissociation and C–S bond cleavage, whereas the two catalysts are comparable for the sulfur removal step. Further analysis suggests that the behavior of the Ti_8C_{12} nanoparticle is associated with its unique structure.

II. Theoretical Methods

Calculations were performed using all-electron DFT with the DMol³ code.¹⁴ A numerical basis set of accuracy comparable to a Gaussian 6-31G (d) basis, with a local basis cutoff of 5.5 Å, and the GGA-RPBE functional¹⁵ to describe the exchange

and correlation were utilized. The procedure for the calculations is outlined in detail in refs 8 and 9. In accordance with previous studies,^{1,3,8,9} Ti_8C_{12} begins in a T_d -like C_1 structure that includes four low-coordinated Ti° , four high-coordinated Ti^{I} and six C_2 groups (1, Figure 1). Transition states here were identified using the combination of synchronous transit methods and eigenvector following, and verified by the presence of a single imaginary frequency from a sequential vibrational frequency analysis.

III. Results and Discussion

Figure 1 shows different steps for the HDS of thiophene ($\text{C}_4\text{H}_4\text{S}$), reaction 1, on a Ti_8C_{12} metcar. The HDS process involves the dissociative adsorption of H_2 , the adsorption of $\text{C}_4\text{H}_4\text{S}$, the cleavage of C–S bonds, the hydrogenation and desorption of C_4H_4 fragments, and the removal of S adatoms as gaseous H_2S . Figure 2 displays the calculated potential energy diagram for this catalytic cycle, which is expressed in eV and relative to the metcar, three free H_2 molecules and a $\text{C}_4\text{H}_4\text{S}$ molecule in the gas phase.

Similar to other kinetic studies,^{16,17} the dissociative addition of H_2 was considered here as the start for thiophene HDS ($1 \rightarrow 3$, Figure 1). The availability of hydrogen adatoms is essential for the HDS process.^{7a,12} It has been found that on MoS_2 hydrogen dissociation is always endothermic and presents a high activation barrier,^{17,18} which can be lowered by introducing metal adatoms such as Ni and Co.^{11,19} H_2 dissociation on Ti_8C_{12} has not been studied previously. Our calculations show that H_2 molecules do not adsorb at the Ti sites but *spontaneously* dissociate (i.e., no energy barrier for bond cleavage) at the C_2 sites to form an ethylenic group (2, Figure 1), accompanied by a charge transfer of 0.22e from each H atom to the C atom to which it is bonded. One can see that the C atoms of the metcar are not simple spectators but play an essential and unique role in its reactivity toward H_2 . However, the H adatoms do not bond strongly with the C sites (the adsorption energy is −0.15 eV/ H_2). The Ti° sites are more energetically favorable (3, Figure 1) by 0.52 eV/ H_2 and sequential migration of H atoms to the neighboring Ti° sites is accompanied by a partial electron transfer from Ti° to H (TS1, Figure 3). At this point, each H atom is somewhat hydridic, having a charge of −0.22e. This is in accordance with previous studies in which Ti° sites have been identified as the most active sites in Ti_8C_{12} for a number of adsorbates (CO , NH_3 and H_2O).^{8,9} On this basis, we propose that H_2 possibly follows a $1 \rightarrow 2 \rightarrow 3$ or a direct $1 \rightarrow 3$ pathway (Figures 1 and 2) from the gas phase. According to our calculations, the barriers for both paths are comparable ($E_a =$

* Corresponding authors. E-mail addresses: rodriguez@bnl.gov (J.A.R.); muckerma@bnl.gov (J.T.M.).

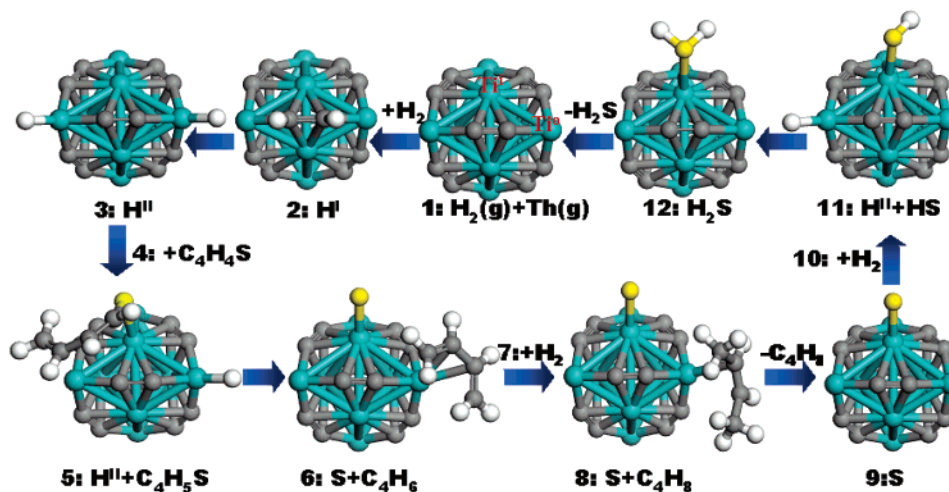


Figure 1. Optimized structures for each step in a catalytic cycle for thiophene (Th) HDS on a Ti_8C_{12} metcar (cyan, Ti; dark gray, C; yellow, S; white, H). H^I and H^{II} correspond to the atomic hydrogen adsorbed at carbon and Ti° sites, respectively.

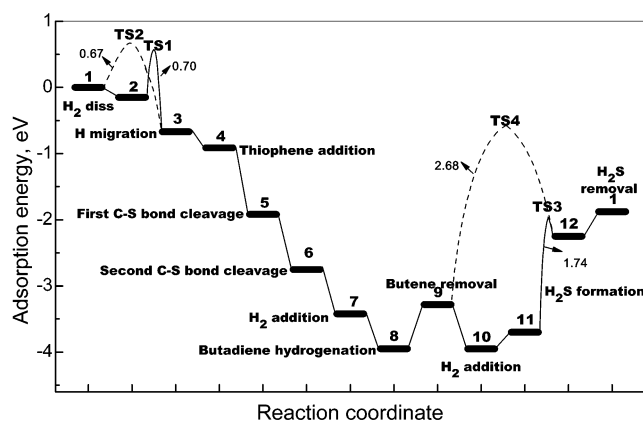


Figure 2. Changes in energy for the HDS of thiophene on a Ti_8C_{12} metcar. The energies in the figure are relative to the Ti_8C_{12} metcar, three H_2 molecules, and a thiophene molecule in the gas phase. The corresponding structures of the intermediates and transition states are shown in Figures 1, 3, and 4.

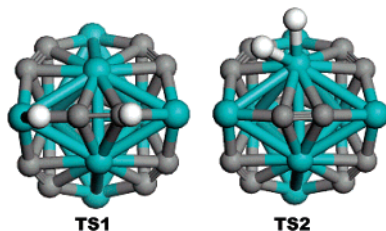


Figure 3. Transition states associated with hydrogen dissociation on a Ti_8C_{12} metcar, “TS1”, and “TS2” in Figure 2 (cyan, Ti; dark gray, C; white, H).

~ 0.7 eV, see transition states in Figure 3). The path $1 \rightarrow 2 \rightarrow 3$ seems more favorable since it first involves a spontaneous dissociation of H_2 . If employing the Arrhenius equation, a barrier of 0.7 eV implies a turnover frequency (TOF) of $\sim 10^8$ at a temperature of 673K, indicating that the formation of atomic hydrogen on Ti_8C_{12} may proceed significantly at HDS operating conditions. It should also be mentioned that H migration to the Ti° site might be aided by quantum mechanical tunneling through the barrier. In the following, we assume that all of the dissociated H adatoms occupy the Ti° sites.

The second important step in the catalytic cycle corresponds to the hydrogenation of thiophene to butadiene ($4 \rightarrow 6$, Figure 1). As illustrated above, the two H adatoms occupy the Ti° sites (3, Figure 1) and become well separated from each other.

Consequently, the simultaneous hydrogenation of both C_α sites in $\text{C}_4\text{H}_4\text{S}$, which has been proposed for HDS on metal sulfides,^{9,18} seems very unlikely. Instead, C_α interacting with the H atoms one after another is found to be highly exothermic (5 and 6, Figures 1 and 2). The adsorbed hydrogen significantly affects the adsorption of thiophene on Ti_8C_{12} . $\text{C}_4\text{H}_4\text{S}$ by itself prefers to adsorb at the Ti° sites (0.4 eV) rather than the Ti^I sites. In the presence of atomic hydrogen, the Ti^I sites (0.83 eV) become more favorable. The $\text{C}_4\text{H}_4\text{S}$ is tethered to a Ti^I site by the S atom (η^1 bonding instead of the η^5 bonding characteristic of thiophene interactions with metal or metal carbide surfaces) with the C_α atoms free to rotate toward a hydrided Ti° site. With one of the H adatoms attacking a C_α atom of $\text{C}_4\text{H}_4\text{S}$, a *spontaneous* cleavage of the first C_α -S bond occurs (5, Figure 1), leading to the formation of the $\text{C}_4\text{H}_5\text{S}$ thiolate (5, Figure 1) and an energy lowering from -0.72 eV to -1.92 eV (Figure 2). Similarly, the cleavage of the second C_α -S bond is also a *spontaneous* process that lowers the energy to -2.75 eV, leaving the adsorbed S atom at a Ti^I site and butadiene at the Ti° site (6, Figure 1). One can see in Figure 2 that the hydrogenated C-S bond cleavage ($4 \rightarrow 6$) is highly exothermic on Ti_8C_{12} ($\Delta E = -1.84$ eV). In contrast, our calculations show that C-S cleavage without prehydrogenation seems less favorable ($\Delta E = -0.55$ eV). In this sense, the hydrogen assists the ring opening of thiophene on Ti_8C_{12} . In the case of MoS_2 , as reported, this process is activated and has a barrier of 1.07 eV.¹⁷ The presence of Ni centers in NiMoS only slightly lowers the barrier to 0.85 eV, a value estimated from an experimental kinetics study.²⁰ Thus, Ti_8C_{12} should be better than NiMoS for C-S bond cleavage.

The third important step in the catalytic cycle includes hydrogenation of butadiene and removal of butene ($6 \rightarrow 9$, Figure 1). To start, an additional H_2 molecule is released and dissociates directly on the Ti° sites ($6 \rightarrow 7$, Figure 1). It has been pointed out that the hydrogenation of butadiene to butenes and butanes is an easy step in the kinetics of HDS.^{7a,12} As shown in Figure 1b, our calculations also show that this reaction ($6 \rightarrow 8$, Figure 1) is highly exothermic ($\Delta E = -1.2$ eV). Accordingly, the detailed kinetics of the hydrogenation of butadiene are ignored in this study, however, the removal of butene from the Ti° site is endothermic ($\Delta E = 0.67$ eV) (9, Figure 2).

The last important step in the catalytic cycle is the removal of sulfur in the form of gas-phase H_2S . It involves (Figure 1) the dissociative addition of an H_2 molecule on a Ti° site (10, Figure 1), the formation of H_2S (11 and 12, Figure 1) and the

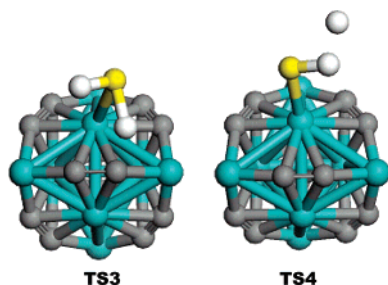


Figure 4. Transition states associated with the hydrogenation of a S adatom or formation of H_2S on a Ti_8C_{12} metacar, “TS3”, and “TS4” in Figure 2 (cyan, Ti; dark gray, C; yellow, S; white: H).

removal of H_2S . After completion, the free metcar catalyst is regenerated (1, Figure 1). As shown in Figure 2, this ($9 \rightarrow 1$) is the most difficult step of all. It costs 1.41 eV in energy with most of this energy being required for the formation of H_2S ($9 \rightarrow 12$, $\Delta E = 1.04$ eV). In contrast, the removal of H_2S is relatively facile ($12 \rightarrow 1$, $\Delta E = 0.37$ eV). Two possible paths were considered for the most endothermic process $9 \rightarrow 12$ (Figure 1). One is $9 \rightarrow 10 \rightarrow 11 \rightarrow 12$ (Figure 1), and the other corresponds to $9 \rightarrow 12$ (Figure 1), the direct formation of H_2S at S sites, since the sulfur dimer at Mo edges of MoS_2 nanoparticles was found to be able to dissociate H_2 molecules.^{16,17} For the first, three-step path, $11 \rightarrow 12$ is the most endothermic step ($\Delta E = 1.46$ eV, Figure 2), having a stretched transition state (TS3, Figure 4) and an activation barrier of 1.74 eV. The other two steps ($9 \rightarrow 10$ and $10 \rightarrow 11$) are either exothermic ($\Delta E = -0.67$ eV for H_2 dissociative addition) or less endothermic ($\Delta E = 0.25$ eV for the formation of HS_{ads}) and, therefore, exhibit a lower barrier. Following the latter path, the barrier becomes as high as 2.68 eV, corresponding to an even more stretched transition state (TS4, Figure 4). This indicates that H_2 dissociation by a single sulfur atom is very unlikely and should be ruled out. The reaction $11 \rightarrow 12$ (Figures 1 and 2) then becomes the rate-limiting step for thiophene HDS on Ti_8C_{12} ($E_a = 1.74$ eV). In the case of sulfides, H_2 dissociation has been found to be the slow step for S removal.¹¹ A reaction energy of ~ 1.2 eV has been estimated for the case of NiMoS from experiment.²⁰ Accordingly, in terms of reaction energy, S removal from both NiMoS (1.2 eV) and Ti_8C_{12} (1.41 eV) is energetically comparable. The difference is that for Ti_8C_{12} , the formation of H_2S from HS_{ads} becomes the slow step in this process. Therefore, similar to NiMoS , the high barrier of the sulfur removal from Ti_8C_{12} can be overcome under real HDS conditions and the S-poisoning should not be very serious.

The catalytic behavior of Ti_8C_{12} for HDS is associated with its unique structure that is quite different from the structures of the bulk materials.^{8,9} Our previous DFT studies^{8a,9} show that the favorable overlap between the π orbitals of the C_2 groups and the s, p, and d orbitals of Ti gives rise to strong bonding in Ti_8C_{12} . As a result, this nanoparticle maintains its geometry and composition during the whole HDS process (Figure 1). In addition, Ti_8C_{12} can also display a high activity due to the presence of corner or edge sites, Ti° sites at corners and C sites at edges (1, Figure 1). The special geometry of Ti_8C_{12} attenuates the ligand effect of C on metal atoms, and the nanoparticle is able to spontaneously dissociate H_2 and hydrogenate thiophene. In this respect, a high carbon/metal ratio does not necessarily imply a low chemical or catalytic activity. The high-coordinated Ti° sites (1, Figure 1), on the other hand, are less active owing to a downward shifted d-band.^{8,9} However, our calculations show that they also facilitate the catalytic reaction by specifically providing a moderate bonding toward the sulfur, thiolate, and

H_2S intermediates. With these two different kinds of sites, Ti_8C_{12} exhibits clear advantages for thiophene HDS in terms of stability, activity, and selectivity.

Here, we have kept the kinetic model as simple as possible by considering thiophene HDS on a clean Ti_8C_{12} nanoparticle. Some other issues that are important for the practical application of metcars in HDS will be considered in a future study. For instance, in some situations, the corner and edge sites may be capped by active molecules from the environment,^{1,8,21,22} which may hinder or slow reaction with H_2 and thiophene. Ti_8C_{12} is sensitive to oxygen and, thus, it is not easy to prepare large macroscopic amounts of this material.^{1,2} We have found that the reactivity of Ti_8C_{12} is retained upon interaction with an oxide support.¹⁰ We plan to investigate the interaction of Ti_8C_{12} with dimethyl-thiophene to establish whether the metcar might be an active catalyst for deep HDS.

IV. Conclusions

In summary, the elementary reaction steps and barriers for thiophene HDS on Ti_8C_{12} were determined using DFT calculations. Our results suggest that Ti_8C_{12} can be an active HDS catalyst. A spontaneous dissociation of H_2 and a spontaneous C–S bond cleavage were observed on Ti_8C_{12} , while both have been identified as activated processes in the case of NiMoS HDS catalysts. The rate-limiting step for HDS on Ti_8C_{12} is the removal of sulfur, where the reaction energy is comparable to that of NiMoS .

Acknowledgment. This research was supported by the U.S. Department of Energy, Division of Chemical Sciences, under Contract DE-AC02-98CH10886.

References and Notes

- (1) Rohmer, M. M.; Benard, M.; Poblet, J. M. *Chem. Rev.* **2000**, *100*, 495.
- (2) Leskiw, B. D.; Castleman, A. W. *C. R. Physique* **2002**, *3*, 251.
- (3) Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1993**, *115*, 11165.
- (4) Van Heijnsbergen, D.; Duncan, M. A.; Meijer, G.; von Helden, G. *Chem. Phys. Lett.* **2001**, *349*, 220.
- (5) Li, S.; Wu, H. B.; Wang, L. S. *J. Am. Chem. Soc.* **1997**, *119*, 7417.
- (6) Dance, I. *J. Am. Chem. Soc.* **1996**, *118*, 6309.
- (7) Furimsky, E. *Appl. Catal. A: General* **2003**, *240*, 1. (b) Chen, J. G. *Chem. Rev.* **1996**, *96*, 1447.
- (8) Liu, P.; Rodriguez, J. A.; Hua, H.; Muckerman, J. T. *J. Chem. Phys.* **2003**, *118*, 7737. (b) Hou, H.; Muckerman, J. T.; Liu, P.; Rodriguez, J. A. *J. Chem. Phys. A* **2003**, *107*, 9344.
- (9) Liu, P.; Rodriguez, J. A. *J. Chem. Phys.* **2003**, *119*, 10895.
- (10) Our DFT calculations indicate that a Ti° site of Ti_8C_{12} bonds to a surface oxygen atom of MgO (bond energy ca. 2.14 eV) in such a way that the base plane of the outer tetrahedron is roughly parallel to the surface. The Ti_8C_{12} does not undergo a structural transformation, and its chemical activity remains virtually unchanged.
- (11) Rodriguez, J. A.; Hrbek, J. *Acc. Chem. Res.* **1999**, *32*, 719.
- (12) Topsøe, H.; Clausen, B. J.; Massoth, F. E. *Hydrotreating Catalysis: Science and Technology*; Springer: New York, 1996.
- (13) Liu, P.; Rodriguez, J. A. *Catal. Lett.* **2003**, *91*, 247.
- (14) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508; *J. Chem. Phys.* **2000**, *113*, 7756.
- (15) Hammer, B.; Hansen, L. B.; Nørskov, J. K. *Phys. Rev. B* **1999**, *59*, 7413.
- (16) Neurock, M.; van Santen, R. A. *J. Am. Chem. Soc.* **1994**, *116*, 4427.
- (17) Lauritsen, J. V.; Nyberg, M.; Nørskov, J. K.; Clausen, B. S.; Topsøe, H.; Lægsgaard, E.; Besenbacher, F. *J. Catal.* **2004**, *224*, 94.
- (18) Bollinger, M.; Jacobsen, K. W.; Nørskov, J. K. *Phys. Rev. B* **2003**, *67*, 85410.
- (19) Rodriguez, J. A. *J. Phys. Chem. B* **1997**, *101*, 7524.
- (20) Borgna, A.; Hensen, E. J. M.; van Veen, J. A.; Niemantsverdriet, J. W. *J. Catal.* **2004**, *221*, 541.
- (21) Selvan, R.; Pradeep, T. *Chem. Phys. Lett.* **1999**, *309*, 149.
- (22) Cartier, S. F.; Chen, Z. Y.; Walder, G. J.; Sleppy, C. R.; Castleman, A. W. *Science* **1993**, *260*, 195.