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Application of Topological Analysis of the Electron Localization Function to the Complexes of Molybdenum Carbide Nanoparticles with Unsaturated Hydrocarbons

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Abstract

The catalytic transformation of the heavy aromatics in bitumen into lighter components is the key to the upgrading and refining of the oil sands. To understand the chemical bonding in molybdenum carbide nanoparticle (MCNP) catalysts and the chemisorption bonds between the MCNPs and unsaturated hydrocarbons, the topological analysis of the electron localization function was applied to various MCNPs and their complexes with unsaturated hydrocarbons. For some of the smaller complexes comparisons are made with the Atoms-in-Molecules approach, including the calculation of delocalization indices. The results are interpreted in the Lewis bonding scheme. It was found that the Mo-C bonding can be highly ionic in cases like Mo_8C_{12} and MoC , but shows significant covalent character in Mo_2C , Mo_3C , and $\text{Mo}_{28}\text{C}_{14}$. The chemisorption bonds between hydrocarbons and the MCNPs involve electron sharing of various types with strong covalent character. The strong three- or four-center interactions determine the adsorption configurations of the hydrocarbons on the molybdenum carbide nanoparticles. Derivatives of benzene show some different bonding features, which depend strongly on the substituent or the heteroatom.

Keywords: Molybdenum Carbide Nanoparticles; Unsaturated Hydrocarbons; ELF; AIM; Chemisorption

Introduction

In the petrochemical industry, the catalytic transformation of the heavy aromatics in bitumen into lighter components is the key to the upgrading and refining of the oil sands.¹ In particular, the development of cheap nano catalysts for the “*in-situ*” upgrading of oil sands has attracted much attention.² Of special interest is molybdenum carbide, which is known as an economical substitute for noble metals as hydrotreating catalysts.^{3,4} Hydro-treating involves multiple reactions⁵: the removal of impurities (N, S) are called hydrodesulphurization (HDS) and hydrodenitrogenation (HDN); the increase of the hydrogen/carbon (H/C) ratio is called hydrogenation (HYD); and the breaking of C-C bonds is called hydrocracking (HYC).

The catalytic properties of materials are determined by their electronic structures.⁶ In order to understand the catalytic behavior of molybdenum carbide nanoparticles (MCNPs) for reactions such as hydrogenation, it is necessary to understand the electronic structure of this system, including the bonding in the MCNPs and the bonding between the adsorbents and the MCNPs. Adsorption is usually known as a local phenomenon. But how “local” is it in terms of electronic structure? How do various unsaturated hydrocarbons bond with the MCNPs? For hydrocarbons adsorbed on MCNPs, there are two types of Mo-C bonds: those between the Mo and C in the nanoparticle, and those between the Mo in the nanoparticle and the C of the hydrocarbon on the surface. An interesting question comes naturally: how different are

those two types of Mo-C bonds?

In quantum mechanics, the movement of electrons does not have a boundary. To define an atom or a bond requires the dividing of space in a chemically meaningful way. One way to define atoms and bonds in molecules unambiguously is the atoms in molecules (AIM) theory introduced by Bader. In his original work⁷, Bader used the topology of the electron density (ρ) and the analysis of critical points of ρ to classify atoms and bonds. A critical point (CP) of a scalar function is a point in 3-dimensional space where the first derivative of the function is zero. CP analysis classifies the CPs with the signs of their curvatures. Based on the AIM theory, atoms and bonds in the molecules are indicated by nuclear critical points and bond critical points. Similar topological analysis can be applied to the molecular electrostatic potential (MEP)⁸⁻¹¹, the Laplacian of the electron density ($\nabla^2\rho$)¹² and the electron localization function (ELF).¹³

It is well known that electron delocalization is important for aromaticity. In addition, electron delocalization has been shown to be useful in explaining the nature of chemical bonding in transition metal complexes¹⁴. The ELF is a property introduced by Becke and Edgecombe¹⁵ for the evaluation of the localization of electrons in molecules. Compared to AIM and MEP, it directly reveals the Pauli exchange repulsion effect by measuring the excess of local kinetic energy due to Pauli repulsion, which is fundamentally important for chemical bonding in valence-shell electron-pair repulsion (VSEPR) theory¹⁶. Besides, the Laplacian of the electron density does not fully reveal

the shell structure of heavy atomic systems.¹² The ELF can be written as:

$$\text{ELF} = \left[1 + \left(\frac{D}{D_h} \right)^2 \right]^{-1} \quad (1)$$

where

$$D = \frac{1}{2} T_s - \frac{1}{8} \frac{|\nabla \rho|^2}{\rho} \quad (2)$$

$$D_h = \frac{3}{10} (3\pi^2)^{5/3} \rho^{5/3} \quad (3)$$

In equation (2), T_s is the kinetic energy density. D represents the curvature of the electron pair density for electrons of the same spin. D_h is the corresponding expression for the homogenous electron gas of the same density. ELF has values between 0 and 1. Values close to 1 indicate electron pairing or fully localized electrons; values close to zero means completely delocalized electrons. If, at a certain position, $D=D_h$ and $\text{ELF}=0.5$, then the Pauli repulsion at that position is equal to the Pauli repulsion of the homogeneous electron gas of the same density. The topological analysis of ELF was first introduced by Silvi and Savin for the classification of chemical bonds¹³. It provides a basis for the understanding of chemical bonding in the Lewis bonding scheme. Soon, the classification of chemical bonds in the framework of ELF was applied to the bonding analysis of molecules¹⁷, small alkali metal clusters¹⁸ and crystalline materials¹⁹. Kohout et al.²⁰ first applied ELF to transition metal systems and suggested that the atomic core regions are necessary to describe the detailed bonding situation. The ELF analysis of the nature of metal-carbon bonding in MCH_1 , MCH_2 , MCH_3 molecules by Vidal et al.²¹ shows an almost pure ionic bond for all the systems studied with $\text{M:C}=1:1$, including $\text{M} = \text{K}, \text{Ca}, \text{Sc}, \text{Ti}, \text{V}, \text{Cr}$ and Mn cations.

Similar analysis²² shows the nature of the chemical bond in di-metallic complexes as a resonance interaction due to the d electrons fluctuating within the core basins of the metal centers, and tri- and tetra-metallic complexes as multi-center bonding among the metal atoms indicated by the valence basin among the metallic centers. A recent review¹⁴ by Matito and Solà covers the theory and application of ELF in transition metal complexes. However, to our knowledge, there is still no reported work that applies ELF analysis to transition metal clusters or the bonding of transition metal clusters with small molecules.

Previously when we compared the bonding of benzene on Pt(111) and Mo₂C(0001), the geometry showed di- σ and π bonds for Pt, while it showed three σ bonds for Mo₂C²³. However, it is still not clear what caused these differences. In the explanation of surface bonding between metal clusters and organic molecules, the most popular model²⁴ is that based on the molecular orbital theory: the donation of molecular π electrons into the metal d orbitals and the back donation to the molecular π^* orbital. The molecular orbital diagrams, however, become too complicated when many atoms in a nanoparticle are involved, especially with many heavy transition metal atoms that are rich in d electrons. The band structure theory is restricted to bulk solids with an infinite number of atoms, and ignores quantum size effects. Therefore neither of the two methods is very suitable for studying the electronic structure of clusters or nanoparticles. Herein, we use the ELF topological analysis based on DFT molecular orbital theory, and then we use the Lewis bonding scheme to explain the bonding in the

MCNPs, as well as the surface bonding between the MCNPs and various unsaturated hydrocarbons. For some of the smaller complexes comparisons are made with the Atoms-in-Molecules approach, including the calculation of delocalization indices. The understanding of these bonding interactions may help the construction of future multi-scale models and the interpretation of the results from multi-scale simulations. We first examine the bonding in small molybdenum / molybdenum carbide molecules (MoC , Mo_2 , Mo_2C , Mo_3C), then extend the study to larger cluster models resembling the MCNPs (Mo_8C_{12} and $\text{Mo}_{28}\text{C}_{14}$). Then in the next section, we look at the complexes of these systems with unsaturated hydrocarbons, starting from the smallest system in this category: the ethylene molecule adsorbed on Mo_2C . Then we go to a slightly larger system: a C_6H_6 molecule on Mo_3C . In both cases, we also studied their bonding on a $\text{Mo}_{28}\text{C}_{14}$ MCNP for comparison. Afterwards, we move on to heterocyclic compounds pyridine and thiophene on the $\text{Mo}_{28}\text{C}_{14}$ MCNP. For even larger molecules like naphthalene or toluene, we studied their bonding with a slightly larger $\text{Mo}_{38}\text{C}_{19}$ MCNP. We use the same nomenclatures for the sites of the MCNPs as in our previous work²³: Hm site, Hc site, and Vc site, which indicate there is a Mo atom, a C atom, and a vacancy underneath a Mo-Mo-Mo three-fold hollow site, respectively.

Computational Methods

The electronic structure calculations were performed with the linear combination of Gaussian-type orbital Kohn-Sham density functional theory (LCGTO-KS-DFT) package deMon2k²⁵ within the GGA-PBE²⁶ formalism. The

all-electron basis set DZVP and the GEN-A2 auxiliary set²⁷ were used for all atoms. The structures of all systems were optimized; however, for Mo₂₈C₁₄ and Mo₃₈C₁₉ MCNPs, the boundary atoms are fixed while the rest are allowed to relax, the same way they were used previously for adsorption studies.²³ ELF was calculated from an all-electron basis set, because as Kohout²⁰ pointed out, the “valence ELF” calculated from valence electrons does not have a clear physical meaning, and the analysis of ELF needs to involve the atomic core regions. The wavefunctions of the systems were then passed to the Dgrid²⁸ program for the calculation of ELF and the integration of the electron density in the ELF basins. A mesh size of 0.05 Bohr and a border of 6.0 Bohr was used for the ELF calculations for the integration of the electron density. The 3D figures of ELF were plotted with the ParaView²⁹ package. For visualization purposes only, separate ELF calculations were performed with a mesh size of 0.1 Bohr to avoid the overload of system memory.

In the ELF topological analysis, the local maxima of the function are defined as localization attractors. Each attractor is contained in a basin, which can be either a core basin, or a valence basin; a valence basin is further categorized as a bonding basin or a non-bonding basin. A core basin contains a nucleus, while a valence basin (denoted “V”) connects a number of core basins. This number is usually called the synaptic order of a valence basin, and is determined by the number of core basins which share a common boundary with it. Two-center bonds are characterized by V(X, Y) disynaptic basins, tri-center bonds by V(X, Y, Z) trisynaptic basins, and so on. All the core basins

are marked as “C(X)”, where “X” is the atom name.

For the visualization of the ELF in the figures, the isosurface of the ELF in 3D space are plotted. The value of the isosurface is called “ η ELF”. To visualize the inside of the isosurfaces, a surface or “clip” cuts through the isosurfaces. A clip is an intersection of the whole isosurface, usually at half space, which removes the geometry on one side of the middle plane. Clips are created because the isosurfaces are closed, which prevents the visualization of the inner regions inside the basins. On a clip, ten contour curves of ELF are included. The difference in ELF between contours on a clip is 0.05, which is indicated as Δ ELF=0.05 on the figures. All the valence basins are marked as “V(mX, nY)”, where “X” and “Y” are the names of the elements, and m and n are the number of the corresponding atoms that are involved in the bonding. The integration of electron density in the ELF basins are labeled on the figures or shown in tables. Because of the sizes of the systems and the complexity of the ELF isosurfaces for the large nano-scale systems, a lot of different subtle rotations have to be performed to visualize all the chemically important basins. To avoid too many figures, the ELF isosurfaces are rotated in a way to balance the visualization of different basins, however with all the detailed information provided in tables.

The quantum theory of atoms in molecules (QTAIM) results were calculated and visualized using the AIMALL³⁰ program suite. The properties considered are the QTAIM basin population (N), net charge (q), localization index (λ), percentage of localization with respect to the basin population (% λ), and electron

delocalization indices $\delta(X, Y)$ for atoms X and Y.

Results

1. *The bonding in Molybdenum Carbides and MCNPs*

1.1 MoC

The ground state of MoC was found to be $^3\Sigma^-$, with a bond length of 1.691 Å, close to the spectroscopic^{31,32} and multireference configuration interaction (MRCI)³³ value of 1.688. The multi-configurational self-consistent field (CASSCF) and MRCI calculations³³ have predicted the ground state of MoC to be $^3\Sigma^-$ with a $10\sigma^2 11\sigma^2 5\pi^4 2\delta^2$ configuration. There is only one disynaptic bonding attractor between Mo and C, located 0.624 Å from Mo and 1.067 Å from C, with a basin population of 0.2e (Fig. 1a). The position of the ELF basin attractor is very similar to the location of the Mo-C bond critical point from QTAIM, which is 0.676 Å from Mo and 1.015 Å from C (Fig 1b). The C core basin plus its lone pair basins together have 7.5e. The low population in the valence basin between Mo and C reflects the ionic character of the bonding of MoC³⁴. This is also reflected by the results from the AIM analysis. As shown in Table 1, Bader⁷ population analysis shows a net charge of about +0.6 e for Mo and -0.6e for C, indicating a strong ionic interaction. Second, the delocalization index from QTAIM shows that there are 3.261 e delocalized between the C and Mo atoms. The delocalization index³⁵ is a measure of the number of electrons that are shared or exchanged between atoms, and is related to the bond order. The inconsistency

between the ELF basin population and the QTAIM delocalization index has been reported by Chesnut et al before^{36,37}, and was explained as being due to polarization effects³⁷.

1.2 Mo₂

The ground state of Mo₂ is $^1\Sigma_g^+$, in agreement with the spectroscopic study³⁴. The bond length of Mo₂ was found to be 2.021 Å, slightly larger than the experimental value of 1.938 Å³⁴. As Fig. 2 shows, it has two ring-shaped disynaptic basins between the Mo atoms, and another two monosynaptic bow-shaped basins at each end outside the molecule. The inner ring basin contains 3.0 e, and the outer ring basin contains 0.5 e. The total bonding basin population of 3.5 e is very close to the value of 3.6 e reported by Michellini et al³⁸. However, instead of two ring basins, only one torus basin was found in their work. Besides, there are two basins between the Mo atoms, each containing 0.8e. According to Kohout and Silvi, there is no further subshell structuring in the ELF partition²⁰; therefore, the di-synaptic basin formed by the 3d electrons are also valence basins. Altogether, 5.1e were found in the bonding basins of Mo₂. In addition, we point out the existence of the two monosynaptic bow-shaped basins on each side of the Mo atoms, corresponding to the V(Mo) basin. However, only 0.35 e was found in each of these V(Mo) basins. If we follow the definition of Michellini et al³⁸, and include the 3d basins between the Mo atoms with 0.8 e, and the non-bonding outer basins with 1.5 e and 0.3 e, then the total population of V(Mo) comes to 2.95 e, and is roughly compared to the 3.2 e reported by Michellini et al.

Comparing the percentage of localization with respect to the basin population (% λ) of the Mo atoms, we can see that the electrons of the Mo atoms in MoC (92%, Table 1) are less localized than the Mo atoms in Mo₂ (96%, Table 2), consistent with the delocalization indices (3.3 and 6.1, respectively).

1.3 Mo₂C

In its singlet ground state, the ELF topology of Mo₂C is presented in Fig. 3. The two disynaptic basins between the two Mo atoms remain, but each has only 0.7 e, slightly lower than that of Mo₂. The inner and outer ring basins of Mo₂ became two half-ring basins, containing 0.6 e and 0.3 e, respectively. The two non-bonding monosynaptic bow-shaped basins at the end outside of Mo₂ also remain, indicating the bonding of Mo-C in Mo₂C does not involve the Mo 5s nonbonding electrons. In total, the bonding basins of Mo-Mo contain 2.3 e, showing a decrease of 2.8 e compared to Mo₂ (5.1 e), which leads to the weakening of the Mo-Mo bond. The majority of the loss comes from the ring basins in Mo₂. The two bonding basins of Mo-C contain 1.8 e each. Compared to the 0.2 e in MoC, which shows significant change of the Mo-C bond from an ionic character in MoC to more covalent character in Mo₂C. However, QTAIM results (Table 3) show that the delocalization index of the Mo-C bond decreases from 3.26 in MoC to 1.70 in Mo₂C, indicating the overall weakening of the Mo-C bond from MoC to Mo₂C. A similar decreasing of the delocalization index was found for the Mo-Mo bonds on going from Mo₂ to Mo₂C.

As far as multi-center bonding is concerned, the QTAIM method shows a

ring critical point among the Mo-Mo-C ring; however, no tri-synaptic bonding basin was found with the ELF method.

1.4 Mo₃C

In its triplet ground state, Mo₃C has a pyramidal structure with C1 symmetry. Its ELF topology can be seen as two Mo₂C moieties sharing a Mo-C edge. The bonding of Mo1-Mo2 and Mo1-Mo3 both retain two ring-shaped basins as can be seen from the contour slice (Fig. 4). However, they are not of the same strength; in fact the Mo1-Mo3 bond is significantly stronger than Mo1-Mo2. The bonding of Mo2-Mo3 does not have ring basins, but the disynaptic basin contains 2.8 e. C-Mo2 and C-Mo3 are of the same strength; both of them have 1.3 e in their disynaptic basins.

1.5 Mo₈C₁₂

The Mo₈C₁₂ MCNP is usually referred to as a “metcar”³⁹. Our calculation shows that Mo₈C₁₂ has a tetrahedral-like structure (Fig. 5a), in agreement with previous DFT calculations³⁵. There are two types of Mo atoms, the vertex (outer) ones (Mo^o) and the face (inner) ones (Moⁱ). The topology of the ELF isosurface for Mo₈C₁₂ (Fig. 5b) shows groups of disynaptic valence basins, including V(C, C), V(C), and V(Moⁱ, Moⁱ); others correspond to the C and Mo core basins, and multi-center basins. The Mo₈C₁₂ MCNP can also be seen as an inner tetrahedron (Moⁱ)₄ capped by an outer tetrahedron (Mo^o)₄. The inner tetrahedron (Moⁱ)₄ involves three types of bonds (Table 4): six

V(2Mo) two-center interactions, four V(3Mo) three-center interactions, and one V(4Mo) four-center interactions. The attractors of these basins are shown in Fig. 6. The six two-center attractors are located on the edges of the inner tetrahedron (in green); the four three-center attractors are on the faces of the inner tetrahedron (in ochre), and only four-center attractors are located in the geometric center of the inner tetrahedron (in black). The four Mo atoms in the outer tetrahedron (Mo^0)₄ are connected by 6 C-C units. The bonding between the (Mo^0)₄ atoms and the C atoms of C-C units are ionic, as there is no valence basin between them. The C-C bonding basin has about 2.9 e, indicating a bond order of 1.5.

1.6 Mo₂₈C₁₄

There are two flat surfaces on the Mo₂₈C₁₄ MCNP (Fig. 7a), and we will focus on the Mo-terminated surface as it is more catalytically active and is the surface of interest in most of the reported studies. Two types of basins were observed: V(3Mo) three-center basins and V(C, 3Mo) four-center basins (Fig. 7b). The V(3Mo) basins are similar to the ones found in the bulk structure of MoS₂. These basins correspond to the Hm and Vc sites on the surface, following the nomenclature in the literature⁴⁰. The V(C, 3Mo) four-center basins are unique for molybdenum carbide, and are quite consistent on all the Hc sites with about 2.6 e in the basins. These sites are made up of a C atom below the hollow of 3 Mo atoms. Due to the distortion of the Mo₂₈C₁₄ MCNP during geometry optimization, one of the Hm sites is reduced to a V(Mo, Mo) two-center basin.

2. Complexes of MCNPs with unsaturated hydrocarbons

2.1 $\text{Mo}_2\text{C}-\text{C}_2\text{H}_4$ complex

In its singlet ground state, the $\text{Mo}_2\text{C}-\text{C}_2\text{H}_4$ pair is not planar. The lower C from Mo_2C (C3 in Fig. 8) is out of the plane made by the Mo-Mo-C-C four member ring. Two two-center interactions between the Mo atoms and the C1 and C2 atoms of C_2H_4 can be readily recognized as 2 Mo-C σ -bonds. The integration of the electron density gives 1.3 e in each of the basins. The strength of Mo bonding with C3 in Mo_2C is similar, with 1.4 e in the basins, showing the similar strength between the chemisorption Mo-C bond and the Mo-C bond in Mo_2C . Upon chemisorption, the evolution of the basin population was observed. Compared to the case preceding adsorption for Mo_2C , upon adsorption there is a decrease of the $V(\text{C3}, \text{Mo})$ population from 1.8 e to 1.4 e.

Comparing the delocalization index of the two type of Mo-C bond in $\text{Mo}_2\text{C}-\text{C}_2\text{H}_4$ (Table 5), the chemisorption type of Mo-C bond is weaker ($\delta=0.81$) than the Mo-C bond in the Mo_2C fragments ($\delta=1.69$). Actually, the latter Mo-C bond has almost the same delocalization index as the Mo_2C molecule itself ($\delta=1.700$).

Interestingly, the ring basin between the two Mo atoms in Mo_2C (and Mo_2) disappeared when C_2H_4 is adsorbed on Mo_2C . The bonding basins between them now have 3.6 e, which is even higher than the situation in Mo_2C (2.3 e, where 0.9 e is from ring basins, and 1.4 e is from other disynaptic bonding basins).

The bonding basin between the two C atoms in C_2H_4 has 2.0 e, indicating the

change from a C=C double bond to a C-C single bond after interaction with Mo₂C. This is validated by the change of C-C bond delocalization index from 1.92 in the free C₂H₄ molecule to 1.12 in the C₂H₄-Mo₂C pair.

2.2 Mo₃C-C₆H₆ complex

The ground state of the Mo₃C-C₆H₆ pair is also a singlet state. However, the optimized structure is far from symmetric. Among the three Mo atoms, C1 is bonded to Mo1 only, with 2.4 e in the bonding basin (Fig. 9). Both C2 and C3 are bonded to Mo3 through two-center interactions, with 2.0 e and 2.9 e in the basin, respectively. C5 and C6 form similar interactions with Mo2, but with much weaker strength. The electron density integrated in these basins is only 0.54 e and 0.74 e. C4 is special in that it does not have any bonding interaction with the Mo atoms.

2.3 Mo₂₈C₁₄-ethene complex

Compared to the two equivalent V(C, Mo) two-center basins (1.3 e) on Mo₂C, upon interaction with the Mo₂₈C₁₄ MCNP, ethene shows a four-center V(C, 3Mo) basin with a population of 1.42 (Fig. 10, and Table 6). The other C forms a two-center basin of 0.98e with a Mo atom. This indicates that the V(C, 3Mo) four-center interaction is stronger than the V(C, Mo) two-center interaction, and is preferred when ethene is moved from Mo₂C to Mo₂₈C₁₄. However, it undermines the strength of the other V(C, Mo) two-center interactions. The C-C valence basin now has 2.13 e, slightly larger than that in Mo₂C.

2.4 Mo₂₈C₁₄-Benzene complex

From now on, when we discuss the ELF of complexes with the benzene molecule, we will always use the same numbering system as in Fig. 11. As Fig. 11 and Fig. 12 show, there are two types of bonding basins between benzene and the Mo₂₈C₁₄ MCNP. One type is the V(C, Mo) two-center basins, and the other is V(C, 3Mo) four-center basins. The V(C, 3Mo) bonding basins contain about twice the electron density as the two-center basins (Table 7). For both Hm and Vc sites, benzene forms two V(C, 3Mo) four-center basins and three V(C, Mo) two-center basins, with the adsorption valence basin V_{ad} containing 4.18 e and 3.54 e, respectively. However, on the Hc site, benzene forms only one V(C, 3Mo) three-center basin, and three V(C, Mo) two-center basins, with the adsorption valence basin V_{ad} containing only 2.78 e.

One of the purposes of this study is to get a deeper understanding of the adsorption phenomenon found in our previous DFT calculations.²³ Our current findings suggest that the lack of one strongly bonding V(C, 3Mo) four-center basin is the reason for the relatively weaker adsorption of benzene on the Hc site, compared to Vc and Hm. This could also be reflected on the C-C bonds of benzene on different sites of the MCNP. The average C-C bonding basins of benzene decreases as: gas phase > Hc > Vc > Hm, indicating the increase of the breaking of the aromaticity of benzene on the MCNP surface. This explains the trend of binding affinity found from other DFT calculations^{23,41}. Comparing the bonding basins formed by Mo and C in the Mo₂₈C₁₄ MCNP (1.4-2.6 e) and the chemisorption basin between Mo in the MCNP and C from

benzene (0.55-1.02 e), we can say that these two types of bonds have quite different strength in terms of electron sharing.

Upon adsorption, the basins on the adsorption sites of the MCNP changed slightly. The V(3Mo) basin on the Vc site increased from 1.25 e to 1.30 e. The V(3Mo) basin on the Hm site decreased from 1.06 e to 1.02 e. The four-center V(C, 3Mo) basin on the Hc site also decreased from 2.82 e to 2.64 e.

To summarize this part, we've successfully explained the relative thermodynamic adsorption strength of benzene on different sites of the (0001) surface of Mo₂C presented in our previous studies.²³ The adsorption phenomenon is dominated by multi-center bonding basins between benzene and Mo₂C. The adsorption strength can also be measured by the destabilization of the benzene molecule, which is indicated by the average of the total electron density in the bonding basins of the C-C bonds in benzene. Considering that the main content of oil sands are substituted polyaromatic hydrocarbons (PAH), in the next part, we will analyze the bonding interactions of different substituted aromatic molecules with MCNPs.

2.5 Mo₂₈C₁₄-Pyridine

Similarly to benzene, pyridine interacts with the Mo₂₈C₁₄ MCNP through two strong V(C, 3Mo) four-center basins and three V(C, Mo) two-center basins (Fig. 13). However, it is interesting that there is no bonding basin between N and Mo, although they align close to each other. Since the basin corresponding to the lone pair in N contains 3.2 e (Table 8), the interactions between the N and Mo are therefore purely

ionic. All the C-C bonds retain their unsaturated nature with 2.3 e - 2.4 e in the bonding basins. The C-N bonds, however, are all single bonds with 2 e in the bonding basins.

2.6 Mo₂₈C₁₄-Thiophene

As Table 9 shows, among the four C atoms in thiophene, the two C atoms (C1 and C4) bonded with S have the strongest interaction with the Mo₂₈C₁₄ MCNP surface, with almost twice the integrated electron density in the corresponding V(C, Mo) bonding basins. Besides the lone pair electrons, sulfur has a four-center V(S, 3Mo) bonding basin with the MCNP surface, showing the partially covalent nature of the interactions (Fig. 14).

2.7 Mo₃₈C₁₉-Naphthalene

The C-C bonds of naphthalene in the gas phase are not equivalent (Fig 15). The four bonds of C1-C2, C3-C4, C6-C7 and C8-C9 are double bonds in two of the three resonance structures of naphthalene, while the other C-C bonds are double bonds only in one of the three resonance structures. However, a redistribution of electrons among the C-C bonds was observed on the MCNP surface. This is indicated by the population in the valence basins of the C-C bonds. Table 10 shows that the average population in the bonding basins of C1-C2, C3-C4, C6-C7 and C8-C9 is 2.41 e, while the average population in the bonding basins of C4-C5, C5-C6, C9-C10 and C10-C1 is 2.46 e. The other three bonds C2-C3, C7-C8 and C10-C5, with 2.74 e in the bonding basins, now become more electron rich than the bonds of C1-C2, C3-C4, C6-C7 and

C8-C9. Comparing the $V(C, C)$ of the benzene and naphthalene on MCNPs, the former shows more single bond nature with fewer electrons in the C-C bonding basins, as the average C-C bonding population is about 2.4 e in benzene and 2.5 e in naphthalene. Also, there is no tetra-synaptic basins between naphthalene and the MCNP; instead, only two trisynaptic ones $V(C, 2Mo)$ were found.

2.8 Mo₃₈C₁₉-Toluene

On the Mo₃₈C₁₉ MCNP surface, toluene forms two $V(C, 3Mo)$ three-center basins and three $V(C, Mo)$ two-center basins (Fig.16), with about the same number of electrons in these two types of basins (Table 11). Compared to benzene, we are mostly concerned about the contribution of the methyl group to the adsorption. As Table 8 and Fig 16 show, neither lone pair electrons nor valence bonding of C in the methyl group with the MCNP was detected, which means there is no direct bonding interaction between the methyl group of toluene and the Mo₃₈C₁₉ cluster. Their interactions are most likely van der Waals in nature. Most of the contribution to the adsorption of toluene on Mo₃₈C₁₉ comes from the C₆ ring. The total population in all the bonding basins between toluene and the Mo₃₈C₁₉ surface ($V_{ad} = 2.73$ e) is equivalent to the Hc site ($V_{ad} = 2.78$ e) of benzene, but significantly less than benzene on Hm ($V_{ad} = 4.18$ e) and Vc sites ($V_{ad} = 3.54$ e). Similar to naphthalene, there is no tetrasynaptic basins found between toluene and the MCNP, but only two trisynaptic basins $V(C, 2Mo)$.

Discussion

The C-Mo bonding in the MoC molecule is largely ionic. For Mo₂C and

Mo₃C, we can rank them following the ionic nature as MoC>Mo₃C>Mo₂C, based on the electronic population in the C-Mo valence basins of 0.2 e, 1.3 e, and 1.8 e, respectively. In the Mo₈C₁₂ nanoparticle, the C atoms form bonds of an ionic nature with the (Mo⁰)₄ atoms, without electrons localized between C and (Mo⁰)₄. Considering that no V(C, Mo) basin was detected in Mo₈C₁₂, we can conclude that the C-Mo bonding in Mo₈C₁₂ has even more ionic character than in MoC. Also, no valence basin between the C atoms and the Mo_{face} atoms was detected. On the Mo-terminated surface of the Mo₂₈C₁₄ MCNP, besides the V(3Mo) basins similar to those in MoS₂, the C atoms also form V(C, 3Mo) four-center basins with three Mo atoms. With 0.7 e - 0.8 e in those V(C, 3Mo) basins, the C-Mo bonding in Mo₂₈C₁₄ has more covalent character than MoC and Mo₈C₁₂, but less than Mo₂C and Mo₃C.

The C-Mo bonding between the hydrocarbons and all the MCNPs show clear covalent character, indicated by the electrons localized between them. Comparing ethene on Mo₂C to Mo₂₈C₁₄, the C-C bonding basin on Mo₂C has 2.0 e, but 2.13 e on Mo₂₈C₁₄, showing that the C=C double bond is more destabilized on Mo₂C. In the Mo₂C-ethene complex, the two types of C-Mo bonds are similar: one is that between ethene and Mo₂C, and the other one is that in the Mo₂C molecule, with 1.3 e and 1.4 e in the bonding basins, respectively. Similar observations can be found when one compares the Mo₃C-benzene and Mo₂₈C₁₄-benzene complexes. In the Mo₂₈C₁₄-ethene complex, the V(C, Mo) two-center basins are similar to the case in the Mo₂C-ethene complex with electron populations decreasing from 1.3 e to 0.9 e. Similar to the C and Mo

multi-center bonding in the $\text{Mo}_{28}\text{C}_{14}$ particle, they are both $\text{V}(\text{C}, 3\text{Mo})$ four-center basins; however, the basin population in the complex is much lower than in the MCNP alone by 1.2 e.

In terms of different unsaturated hydrocarbons, the stronger binding of benzene than polyaromatic hydrocarbons (PAH) such as naphthalene on molybdenum carbide can be explained by the stronger destabilization of the C-C bonds. The average C-C bond after adsorption shows more single bond character in benzene than naphthalene, indicated by the C-C bonding basins.

As Fig. 9 shows, in the $\text{Mo}_3\text{C}-\text{C}_6\text{H}_6$ complex, C2 and C3 both bond to Mo3. According to the definition used in the literature⁴², this would be called a “ π ” bond. However, our results show that there are two separate $\text{V}(\text{C}, \text{Mo})$ bonding basins between each C-Mo pair, showing the character of two σ -bonds. This finding questions the classification of surface bonds into “ π -bond” and “ σ -bond” based on geometric observations in adsorption studies⁴².

The $\text{V}(\text{C}, 3\text{Mo})$ four-center interactions are in general stronger than the $\text{V}(\text{C}, \text{Mo})$ two center interactions, and represent the dominant factor in the interaction of aromatics with the Mo_2C (0001) surface. The reformation of $\text{V}(3\text{Mo})$ three-center basins on the Mo-terminated surface of $\text{Mo}_{28}\text{C}_{14}$ into $\text{V}(\text{C}, 3\text{Mo})$ four-center basins is the dominant factor that affects the binding of hydrocarbons on the $\text{Mo}_{28}\text{C}_{14}$ nanoparticle. It was found in previous studies^{23,41} and in this one that Hc sites are not good for benzene adsorption. This could be well explained by the fact that these sites

already have stable $V(C, 3Mo)$ 4-center basins, and the electrons in the basin shared by these atoms repel the π electrons from unsaturated hydrocarbons.

Conclusions

The main purpose of this paper is to provide a deeper understanding of the adsorption phenomena between unsaturated hydrocarbons and molybdenum carbide nanoparticles, and to explain the trends of adsorption found in our previous work²³. It has been shown that ELF topological analysis is a very useful tool in studying the chemical bonding in MCNPs and their complexes with various unsaturated hydrocarbons. It is able to identify the type of bonding, the strength of the covalent bonds, as well as the atoms involved. The Mo-C bonding can be highly ionic in cases like Mo_8C_{12} and MoC , but shows significant covalent character in Mo_2C , Mo_3C , and $Mo_{28}C_{14}$. The chemisorption bonds between hydrocarbons and molybdenum carbides involve electron sharing of various types of strong covalent character. These bonding interactions on the surface can spread in such a way that three- or four-center interactions are involved. The Mo-terminated surface of the $Mo_{28}C_{14}$ nanoparticle has mainly two types of bonding. One is $V(3Mo)$ three-center interactions, which are also found in Mo_2S ; the other is $V(C, 3Mo)$ four-center interactions located in the “Hc” sites among a C atom and three Mo atoms. These two types of bonding basins define the electronic structure of molybdenum carbide particles. The bonding of unsaturated molecules with MCNPs involves not only Mo-C sigma bonds, but also three- or four-center interactions. These multiple-center interactions are usually stronger than

the Mo-C two-center interactions, and determine the orientation of these molecules on the surface. In terms of covalent bonding, the strength of chemisorption between C from unsaturated hydrocarbons and the MCNPs are very strong, and have similar strength to that of the C and Mo in the MCNPs. Among the substituted aromatics, methyl groups in toluene show no chemical interaction with the MCNP surface, indicating van der Waals type interactions. The N in pyridine interacts with the MCNP surface in an ionic way. The S in thiophene interacts with the MCNP surface with both covalent and ionic character. The extension of the aromatic system from benzene to naphthalene makes the C-C bonds retain more electrons when they are adsorbed on MCNPs.

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Tables

Table 1 QTAIM basin population (N), net charge (q), localization index (λ), percentage of localization with respect to basin population ($\%\lambda$), and electron delocalization indices $\delta(X, Y)$ in MoC

Atom	N	q	λ	$\%\lambda$	Pair	$\delta(X, Y)$
C	6.582	-0.582	4.952	75.232	Mo,C	3.261
Mo	41.418	0.582	39.787	96.064		

Table 2 QTAIM basin population (N), net charge (q), localization index (λ), percentage of localization with respect to basin population ($\%\lambda$), and electron delocalization indices $\delta(X, Y)$ in Mo₂

Atom	N	q	λ	$\%\lambda$	Pair	$\delta(X, Y)$
Mo	42.00	0.00	38.96	92.75	Mo,Mo	6.09

Table 3 QTAIM basin population (N), net charge (q), localization index (λ), percentage of localization with respect to basin population ($\% \lambda$), and electron delocalization indices $\delta(X, Y)$ in Mo₂C

Atom	N	q	λ	$\% \lambda$	Pair	$\delta(X, Y)$
C3	6.67	-0.67	4.98	74.57	C3-Mo1	1.70
					C3-Mo2	1.70
Mo1	41.66	0.34	38.68	92.84	Mo1-Mo2	4.27
Mo2	41.66	0.34	38.68	92.84		

Table 4 The valence basins of Mo₈C₁₂ MCNP and their electronic populations.

Basin	Number	Population
V(C, C)	6	2.9
V(C) _{lp} lone pair	12	3.9
V(Mo ⁱ , Mo ^o)	6	0.30
V(3Mo ⁱ)	4	0.16
V(4Mo ⁱ)	1	0.1

Table 5 QTAIM basin population (N), net charge (q), localization index (λ), percentage of localization with respect to basin population ($\% \lambda$), and electron delocalization indices $\delta(X, Y)$ in $\text{Mo}_2\text{C-C}_2\text{H}_4$

Atom	N	q	λ	$\% \lambda$	Pair	$\delta(X, Y)$
C1	6.298	-0.298	4.207	66.80	C1-Mo1	0.810
					C1-C2	1.124
Mo1	41.341	0.658	38.402	92.89	Mo1-Mo2	3.055
C3	6.761	-0.761	4.991	73.81	Mo1-C3	1.688

Table 6 The ELF basins in the $\text{Mo}_{28}\text{C}_{14}$ -ethene complexes and their electronic populations.

Basin	Population	Basin	Population
V(C1, 3Mo)	1.42	V(C1, H1)	2.12
V(C2, Mo)	0.98	V(C2, H2)	2.04
V(C1, C2)	2.13	V(C3, H3)	2.07
		V(C4, H4)	2.12

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Table 7 The ELF basins in the Mo₂₈C₁₄-benzene complexes and their populations.

<i>Mo₂₈C₁₄-benzene-Hm</i>		<i>Mo₂₈C₁₄-benzene-Vc</i>		<i>Mo₂₈C₁₄-benzene-Hc</i>	
Basin	Population	Basin	Population	Basin	Population
V(C1, Mo)	0.53	-	-	-	-
-	-	V(C2, Mo)	0.61	V(C2, Mo)	0.59
V(C3, Mo)	0.70	V(C3, 3Mo)	1.02	-	-
V(C4, 3Mo)	1.02	V(C4, Mo)	0.55	V(C4, Mo)	0.63
V(C5, Mo)	0.62	V(C5, 3Mo)	0.69	V(C5, 3Mo)	1.00
V(C6, 3Mo)	1.31	V(C6, Mo)	0.67	V(C6, Mo)	0.56
<i>V_{ad}</i>	4.18	<i>V_{ad}</i>	3.54	<i>V_{ad}</i>	2.78
V(C1, C2)	2.73	V(C1, C2)	2.77	V(C1, C2)	2.41
V(C2, C3)	2.50	V(C2, C3)	2.18	V(C2, C3)	2.91
V(C3, C4)	2.28	V(C3, C4)	2.33	V(C3, C4)	2.42
V(C4, C5)	2.35	V(C4, C5)	2.39	V(C4, C5)	2.30
V(C5, C6)	2.29	V(C5, C6)	2.34	V(C5, C6)	2.21
V(C6, C1)	2.21	V(C6, C1)	2.44	V(C6, C1)	2.84
<i>V_{ave}(C, C)</i>	2.39	<i>V_{ave}(C, C)</i>	2.41	<i>V_{ave}(C, C)</i>	2.52

Note: We define V_{ad} as an adsorption valence basin, which refers to the union of all bonding basins between the adsorbent atoms and the cluster atoms; in this case it is the sum of the bonding basins between all C atoms of benzene and the Mo atoms of the MCNP. $V_{ave}(C, C)$ refers to the average of the populations of the six C-C bonding basins in benzene. Gas phase benzene has a $V_{ave}(C, C)$ of 3.0

Table 8 The ELF basins in the Mo₂₈C₁₄-Pyridine complexes and their electronic populations

Basin	population	Basin	Population	Basin	Population
V(C1,3Mo)	0.88	V(C1,C6)	2.4	V(C6,Mo)	0.69
V(C3,3Mo)	1.0	V(C3,C4)	2.4	V(N) lone pair	3.23
V(C4,Mo)	0.6	V(C4,C5)	2.4	V(N,C1)	2.0
V(C5,3Mo)	0.7	V(C5,C6)	2.3	V(N,C3)	2.0

Note: We use the same numbering for the C atoms to their corresponding H atoms as in Fig. 4.12.

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Table 9 The ELF basins in the Mo₂₈C₁₄-Thiophene complexes and their electronic populations

Basin	Population	Basin	Population	Basin	Population
V(C1, Mo)	1.55	V(C1,C2)	2.12	V(S, C1)	1.66
V(C2, Mo)	0.80	V(C2, C3)	2.40	V(S, C4)	1.62
V(C3, Mo)	0.64	V(C3, C4)	2.24	V(S) lone pair	2.54
V(C4, Mo)	1.33			V(S, 3Mo)	1.76

Note: We use the same numbering for the C atoms to their corresponding H atoms as in Fig. 13.

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Table 10 the ELF basins in the Mo₃₈C₁₉-naphthalene complexes and their electronic populations

Basin	Population	Basin	Population	Basin	Population
V(C1, 2Mo)	0.96	V(C1, C2)	2.23	V(C6, C7)	2.56
V(C2, Mo)	0.66	V(C2, C3)	2.77	V(C7, C8)	2.73
V(C4, Mo)	0.75	V(C3, C4)	2.44	V(C8, C9)	2.39
V(C6,Mo)	0.62	V(C4, C5)	2.41	V(C9, C10)	2.51
V(C8,Mo)	0.56	V(C5, C6)	2.44	V(C10, C5)	2.71
V(C9, 2Mo)	0.69	V(C1, C2)	2.56	V(C10, C1)	2.47
V(C10, Mo)	0.15			<i>V_{ave} (C, C)</i>	2.50

Table 11 the ELF basins in the Mo₃₈C₁₉-toluene complexes and their electronic populations

Basin	Population	Basin	Population	Basin	Population
V(C1, 2Mo)	0.57	V(C6, Mo)	0.53	V(C4, C5)	2.44
V(C2, Mo)	0.61	V(C1, C2)	2.44	V(C5, C6)	2.47
V(C4, Mo)	0.59	V(C2, C3)	2.52	V(C6, C1)	2.45
V(C5, 2Mo)	0.43	V(C3, C4)	2.77	V(C7, C3)	2.10

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Figures

Fig. 1 a) The ELF isosurface of MoC at 0.68. $V(C, Mo)$ means the valence basin between C and Mo, and $C(C)$ and $C(Mo)$ indicate a carbon and molybdenum core basin, respectively; b) The QTAIM critical point of MoC; the small dot indicates the position of the critical points in the electron density: green stands for a bond critical point.

Fig. 2 a) The ELF isosurface of Mo_2 at 0.57, with a clip cutting through the centers of the Mo atoms; b) The QTAIM critical point of Mo_2 ; the small dot indicates the position of the critical point in the electron density: green stands for a bond critical point.

Fig. 3 The ELF isosurface of Mo_2C at 0.75, with a clip cutting through the centers of the Mo, Mo and C atoms; b) The QTAIM critical point of Mo_2C ; the small dots indicate the positions of the critical points in the electron density: green stands for bond critical points, and red stands for ring critical points.

Fig. 4 Top and side view of the the ELF isosurface of Mo_3C at 0.57. In the top view, the clip cuts through the three Mo atoms, while in the side view, the clip cuts through two Mo atoms and the C atom.

Fig 5 a) the Mo_8C_{12} particle; the big cyan spheres are Mo atoms and the smaller gray spheres are C atoms. b) the ELF isosurface of Mo_8C_{12} at 0.78; the particle is re-oriented such that one of the outer tetrahedral faces is towards the reader; one of the C, and Mo atoms are labelled in brown color.

Fig. 6 The positions of the attractors of the basins of the inner tetrahedron $(\text{Mo}^i)_4$ in the Mo_8C_{12} MCNP. The Mo atoms are the large cyan balls, and the smaller points are ELF attractors. The two-center attractors are in green, three-center attractors in ochre, and four-center attractors in black.

Fig. 7 a). Top view of the Mo-terminated surface of a $\text{Mo}_{28}\text{C}_{14}$ MCNP; the large yellow balls are Mo, and the smaller brown balls are C. b). The ELF isosurface of $\text{Mo}_{28}\text{C}_{14}$ MCNP at 0.70. For better visualization of the bonding basins below the Mo atoms, a plane cuts through the middle of the top layer of Mo atoms.

Fig. 8 a) The ELF isosurface of the $\text{Mo}_2\text{C}-\text{C}_2\text{H}_4$ pair at 0.77. The ethene molecule is located above, and the Mo_2C molecule is located below. A clip cuts through the two Mo atoms and the two C atoms in ethene; b) The QTAIM critical point of $\text{Mo}_2\text{C}-\text{C}_2\text{H}_4$; the small dots indicate the positions of the critical points in the electron density: green stands for bond critical points, and red stands for ring critical points.

Fig. 9 The ELF isosurface of the $\text{Mo}_3\text{C}-\text{C}_6\text{H}_6$ pair at 0.75. The benzene ring is located parallel to the paper in the front, and the Mo_3C molecule is located with the three Mo atoms also parallel to the paper, but behind it. The C atoms in the benzene ring are numbered in numerical order. The clip cuts through the centers of the three Mo atoms.

Fig. 10 The ELF isosurface of the Mo₂₈C₁₄-ethene pair at 0.70. The clip cuts through the top layer Mo atoms. The Mo₂₈C₁₄ cluster is oriented such that the (0001) plane faces the front. The adsorbed ethene molecule is also parallel to the (0001) plane of the Mo₂₈C₁₄ cluster, with the C and H atoms numbered.

Fig. 11 The ELF isosurface of the $\text{Mo}_{28}\text{C}_{14}$ -benzene pair at 0.75, with benzene on the Hm site. The clip cuts through the first layer Mo atoms. The $\text{Mo}_{28}\text{C}_{14}$ cluster is oriented such that the (0001) plane faces the front. The adsorbed benzene molecule is also parallel to the (0001) plane of the $\text{Mo}_{28}\text{C}_{14}$ cluster, with the C atoms in the benzene ring numbered as shown on the right. The C and Mo core basins with the corresponding atoms involved in the 4-center interaction $V(\text{C}, 3\text{Mo})$ are circled in red.

Fig. 12 The ELF isosurface of Mo₂₈C₁₄-benzene at 0.75, with benzene at the V_c (a) and H_c site (b). The Mo₂₈C₁₄ cluster is oriented such that the (0001) plane faces the front. The adsorbed benzene molecule is also parallel to the (0001) plane of the Mo₂₈C₁₄ cluster, with the C atoms in the benzene ring numbered as shown on the right

side of Fig. 11. The C and Mo core basins with the corresponding atoms involved in the 4-center interaction $V(C, 3Mo)$ are circled in red.

Fig. 13 The ELF isosurface of the $Mo_{28}C_{14}$ -Pyridine complex at 0.70, with the pyridine adsorbed on an Hm site. The $Mo_{28}C_{14}$ cluster is oriented such that the (0001) plane faces the front. The adsorbed pyridine molecule is also parallel to the (0001) plane of the $Mo_{28}C_{14}$ cluster, with the H atoms numbered. The C atoms are numbered in the same order as the corresponding H atoms.

Fig. 14 a) The ELF isosurface of the $\text{Mo}_{28}\text{C}_{14}$ -Thiophene complex at 0.70, with the thiophene adsorbed on a Hm site. The $\text{Mo}_{28}\text{C}_{14}$ cluster is oriented such that the (0001) plane faces the front. The adsorbed thiophene molecule is also parallel to the (0001) plane of the $\text{Mo}_{28}\text{C}_{14}$ cluster, with the H atoms numbered. The C atoms are numbered in the same order as the corresponding H atoms. b) The ELF isosurface of the $\text{Mo}_{28}\text{C}_{14}$ -Thiophene complex at 0.89, with the system reoriented to visualize the $\text{V}(\text{S}, 3\text{Mo})$ basin.

Fig. 15 The ELF isosurface of the $\text{Mo}_{38}\text{C}_{19}$ -Naphthalene complex at 0.70, with naphthalene on the Hm site. The $\text{Mo}_{38}\text{C}_{19}$ cluster is oriented such that the (0001) plane faces the front. The adsorbed naphthalene molecule is also parallel to the (0001) plane of the $\text{Mo}_{38}\text{C}_{19}$ cluster, with the C atoms numbered on the right side.

Fig. 16 The ELF isosurface of the $\text{Mo}_{38}\text{C}_{19}$ -toluene pair at 0.70, with toluene on a Hm site. The $\text{Mo}_{38}\text{C}_{19}$ cluster is oriented such that the (0001) plane faces the front. The adsorbed toluene molecule is also parallel to the (0001) plane of the $\text{Mo}_{38}\text{C}_{19}$ cluster, with the C atoms numbered on the right side.

Graphical Abstract

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