



MODELING CATALYTIC NANOPARTICLES USING MATERIALS STUDIO AND PIPELINE PILOT

Development of new technologies for converting natural gas into liquid hydrocarbons is important for efficient production of chemicals and transportation fuels. Nanoparticles composed of molybdenum and carbon and supported on ZSM-5 zeolites are promising catalysts for natural gas conversion. However the structure of these catalysts and, consequently, the conditions for optimizing their performance are not well understood. Researchers at Stevens Institute of Technology, BIOVIA and Lehigh University have for the first time identified the nanoparticle structures and their anchoring sites using computational tools developed by BIOVIA.

INTRODUCTION

The structure of catalytic nanoparticles is extremely challenging to study experimentally, because nanoparticle size and composition is dynamic under reaction conditions. As a result, we do not know what molybdenum carbide nanoparticles look like and precisely how they fit into the methane catalysis system. This is where materials modeling can play a crucial role and enable development of improved catalytic materials with lower costs and environmental impacts.

Thousands of random nanoparticle geometries were generated with the compositions shown in Figure 1 and subjected to quantum optimization. Sequential generations were 'genetically' selected to obtain the lowest energy structures. The optimized nanoparticles were then placed on zeolite anchoring sites identified by experimental spectroscopic measurements.



Figure 1: Structures of Mo-C nanoparticles and their preferred anchoring sites in a ZSM-5 zeolite support were studied.

This study¹ explains how the structure of a molybdenum carbide nanoparticle changes as a function of its size and C/Mo ratio. It also compares binding of nanoparticles on three different kinds of zeolite anchoring sites, yielding insights on optimization of catalyst formulations and reaction conditions and providing essential information for further studies.

METHOD

All molecular modeling calculations were carried out with various modules within the BIOVIA Materials Studio suite and BIOVIA Pipeline Pilot protocols. Density Functional Theory (DFT) calculations were used to model nanoparticles and nanoparticle-zeolite systems at a quantum mechanical *(ab initio)* level using the GGA RPBE functional, a numerical DNP basis set and semi-core relativistic pseudopotentials. The calculations were carried out in the gas phase using materials models represented by both non-periodic molecular clusters and periodic unit cells.



Figure 2: BIOVIA Pipeline Pilot protocol that runs the genetic algorithm to build and optimize nanoparticles with BIOVIA Materials Studio DMol³ and MaterialsScript.

Initial cluster models of molybdenum carbide nanoparticles anchored on zeolites were validated with multiscale modeling. A hybrid QM/MM (quantum mechanics/molecular mechanics) method was used with periodic zeolite/particle structures to demonstrate that the particle-zeolite clusters were large enough to be sufficiently accurate. The isolated nanoparticles were derived using a genetic algorithm². An initial set of random structures was generated for each particle stoichiometry, and then geometry optimization was performed. The energy of each optimized structure in the first generation was used as a fitness function to select parents, from which the next generation was derived through mutations and matings. This process was iterated until the energy change was less than the selected convergence threshold for 25 consecutive generations.

The software driving these calculations was:

- DMol³ (DFT)³
- QMERA (QM/MM)
- Pipeline Pilot (genetic algorithm)

RESULTS

The most stable structures obtained from the genetic algorithm are shown in Figure 3, and details of the bond distances and angles were reported¹. These are the lowest energy structures by a considerable amount. The next most stable structure of each stoichiometry was higher in energy by 70 kJ/mol or more. In common to all structures is either a 2-Mo or tetrahedral 4-Mo core but with different carbon arrangements, depending on the number of carbon atoms. A two-carbon arrangement is observed for all C/Mo ratios of 1.5 and higher, and a four-carbon chain appears in the case when the C/Mo ratio increases to 3.0.



with a genetic algorithm and DFT geometry optimization calculations.

The anchoring sites for one of the nanoparticles are compared in Figure 4. The energies of the geometry optimized structures were compared to identify which sites and binding modes are the most stable. Anchoring through two Mo atoms was preferred at low C/Mo ratios, but switched to a single Mo atom at higher ratios. Moreover, single Al-atom sites are preferred for these latter cases because binding to double Al-atom sites through a single Mo atom is generally unstable.



Figure 4: Examples of zeolite anchoring sites for the Mo₂C₃ nanoparticle. The particle anchors either to one AI (a,b) or two AI (c,d) atoms via oxygen bridging. Cases where a single Mo atom (a,c) or two Mo atoms (b,d) were compared.

On the external surface of the zeolite, anchoring occurs through silicon atoms and their more flexible OH groups. The Mo_2C_x particles showed a trend of increasing stability with the C/Mo ratio. But only for the highest ratios (≥ 2) do the particles prefer anchoring on Si-atom sites on the external surface to Al-atom framework sites in zeolite pores.

The plot in Figure 5 compares energies of alternate particle geometries in various anchoring scenarios for the Mo_2C_6 stoichiometry. In most cases, the original structure (number 1) is at least 50 kJ/mol more stable. In three cases, the energy was the same. Importantly, only in one case (anchoring on the external surface), was the resulting structure different after optimization. Nanoparticles with 4 Mo atoms exhibited similar trends. These results confirm the validity of the modeling approach.



Figure 5: Relative energies of the best alternative Mo_2C_6 nanoparticle structures anchored on various ZSM-5 sites. The top six structures produced by the genetic algorithm were optimized at each type of anchor site. Structure 1 in each case has a relative energy of zero.



Figure 6: Periodic (a,b) and cluster (c) models of ZSM-5 zeolites. The periodic QM/MM model was used to confirm the results of the 10-T cluster model. The atoms rendered as ball-and-stick were modeled with QM, while the remaining atoms were modeled with MM.

The QM/MM models confirmed the results of the cluster calculations, and provided better energy estimates. A periodic structure of a zeolite with a full unit cell requires significantly more computational resources, but offers more flexibility than a cluster model, which is rigidly constrained at its edges. Therefore, periodic QM/MM models can better account for zeolite relaxation effects due to anchoring of molybdenum carbide nanoparticles and, thus, provide more accurate results.

CONCLUSIONS

Structures of carbon molybdenum nanoparticles and their anchoring sites were identified for the first time. These structures are important in catalytic conversion of natural gas into liquid transportation fuels and chemical feedstocks. All nanoparticles contain a molybdenum core with bridging carbon chains that grow with the C/Mo ratio. Therefore, all nanoparticles have one or two exposed Mo atoms that are available for binding on zeolite anchoring sites.

The results suggest that binding through two Mo atoms is energetically preferable on double Al-atom sites and on external Si sites. But on single Al-atom sites, the binding mode depends on the particle composition. The results also offer insights on how to inhibit migration of nanoparticles to the outer surface of the zeolite – a problem that leads to catalyst deactivation. Molybdenum carbide nanoparticles with C/Mo ratios greater than 1.5 preferentially anchor on external Si sites, which suggests that these particles would tend to migrate from zeolite pores onto the external surface of the zeolite. Therefore, in order to minimize such migration, the C/Mo ratio under hydrocarbon reaction conditions should be maintained below 1.5 with, for example, gas-phase O, or H, treatments.

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