

Supported Molybdenum Carbide Nanoparticles as Hot Hydrogen Reservoirs for Catalytic Applications

Marc Figueras[†], Ramón A. Gutiérrez,^{‡,§} Francesc Viñes,^{*,†} Pedro J. Ramírez,^{§,£} Jose Rodriguez,^{*,‡} Francesc Illas[†]

[†] *Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona. c/ Martí i Franquès 1-11, 08028 Barcelona, Spain.*

[‡] *Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, United States.*

[§] *Facultad de Ciencias, Universidad Central de Venezuela, Caracas 1020-A, Venezuela.*

[£] *Present address: Zoneca-CENEX, R&D Laboratories, Alta Vista, 64770 Monterrey, Mexico.*

*** Corresponding authors:** José A. Rodriguez (rodriguez@bnl.gov), Francesc Viñes (francesc.vines@ub.edu)

Experimental Details

For the preparation of the MoC_y/Au(111) systems, we followed a procedure described in previous studies.^{1,2} The MoC_y nanoparticles were generated by deposition of Mo metal onto a reactive multilayer of ethylene, which was physisorbed on a Au(111) surface at 100 K. Upon heating to 750 K, part of the ethylene desorbed and the MoC_y nanoparticles were left on the gold substrate. These transformations could be followed by using a combination of X-ray Photoemission Spectroscopy (XPS), Temperature Programmed Desorption (TPD), and Scanning Tunnelling Microscopy (STM).¹⁻² In this synthetic approach, it is possible to control the C/Mo ratio in the carbide nanoparticles, and this was varied between 0.6 and 1.1. No signal was observed in the O 1s XPS region indicating that the prepared NPs did not contain oxygen.³ Images acquired by STM showed that the generated nanoparticles were small (0.8-1.5 nm) and grew over the face-centred cubic (*fcc*) troughs located on either side of the elbows of the reconstructed Au(111) substrate.¹

The reactivity of the MoC_y/Au(111) surfaces towards H₂ was examined in a system which combines an Ultra-High Vacuum (UHV) chamber (base pressure $\sim 7 \cdot 10^{-10}$ mbar) and a batch reactor.² Within this system, the sample could be transferred between the reactor and UHV chamber without exposure to air. The UHV chamber was equipped with instrumentation for XPS, Ultraviolet Photoelectron Spectroscopy (UPS), Low-Energy Electron Diffraction (LEED), Ion Scattering Spectroscopy (ISS), and TPD. In

the tests to study the interactions with hydrogen, MoC_y/Au(111) surfaces were positioned in the batch reactor at ~300 K, then 1 Torr of H₂ was introduced for a period of five minutes. After this exposure, the hydrogen gas was removed from the reactor and, through differentially pumped stages, each sample was transferred back to the UHV chamber for surface characterization with XPS and TPD. The samples were free of oxygen and only contained Mo, C, and H on top of the gold substrate.

Computational Details

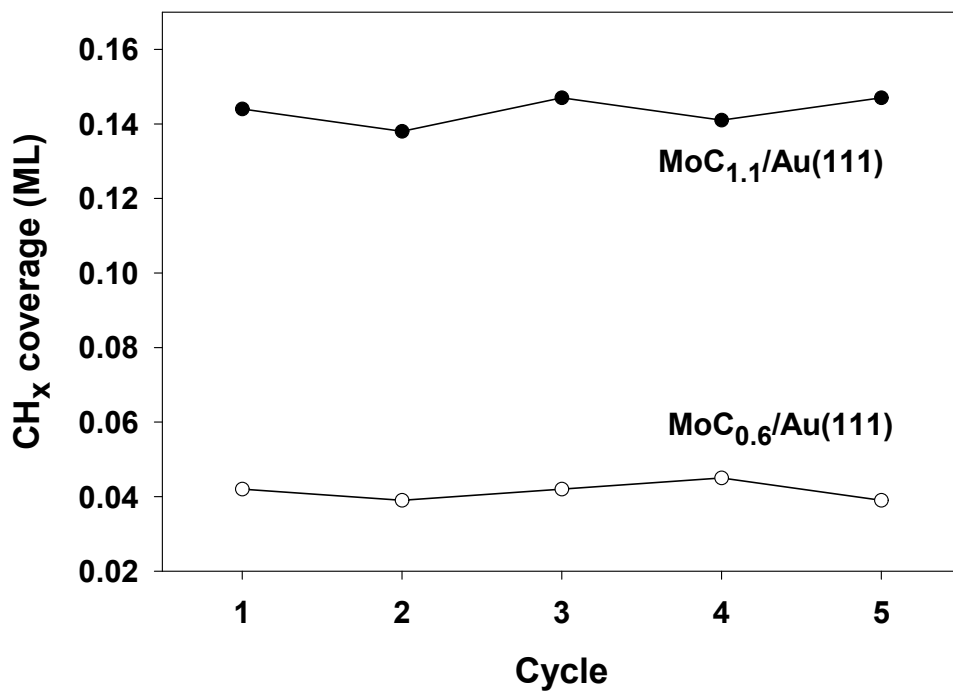
The hydrogen reservoir capabilities on MoC_y/Au(111) has been assessed using a stoichiometric Mo₁₂C₁₂ cluster supported on a Au(111) surface slab model. Such supported nanoparticle structures was obtained and characterized in a previous work,³ obtained first by a thorough search of cluster minima in vacuum, using shape templates from similar TiC compound gained by data mining searches combining interatomic potentials and Density Functional Theory (DFT) calculations,⁴ plus exhaustively sampling the attachment of such clusters on a Au(111) slab model of $p(6\times 6)$ dimensions. The Au(111) slab model is four-layered, where the two upmost layers have been allowed to relax, while the bottommost two layers were kept frozen mimicking the bulk Au environment, *i.e.* 2+2 approach, built and relaxed from a previously optimized Au bulk using the very same computational scheme. Such large dimensions were found to be necessary to properly isolate MoC_y clusters from periodically replicated images, and for the same purpose, a very large vacuum region of 30 Å was added.

The DFT calculations were carried out using the Perdew-Burke-Ernzerhof (PBE)⁵ exchange-correlation (*xc*) functional, adding a dispersive forces treatment by Grimme D3 correction,⁶ already found to be accuracy-wise suited for such systems.³ Spin-polarization was found to be negligible such past studies,³ and so presently not accounted for. The effect of core electrons on the valence electron density has been described by the Projector Augmented Wave (PAW) method of Blöchl,⁷ as implemented in the employed Vienna *Ab-initio* Simulation Package (VASP) code,⁸ as implemented by Kresse and Joubert.⁹ Optimizations were carried out fully relaxing the aforementioned two gold layers, the attached MoC clusters, and the H_x ($x = 1,2$) species upon. The electronic and atomic optimization criteria were set to 10⁻⁵ eV and 0.01 eV·Å⁻¹, respectively, that together with a basis set of plane waves with a kinetic energy limit of 415 eV and a 3×3×1 **k**-point mesh ensure results well within the chemical accuracy of 1 kcal·mol⁻¹, *i.e.* below ~0.04 eV. Transition State (TS) structures were acquired by means

of the Climbing-Image Nudged-Elastic-Band (*CI-NEB*) method,¹⁰ and adsorption minima and TSs were characterized as so by a frequency analysis carried out by Hessian matrix building and diagonalization, constructed by finite differences of 0.03 Å in length.

Several initial geometries were tested for the MoC_y nanoparticle, and the most stable structure was chosen to study the H_x adsorption, the H₂ dissociation, and the H diffusion. The optimization procedure used to gain the minimum energy structure of the nanoparticles was also used to optimize the geometry of the different species adsorbed on the supported nanoparticles. Note that, due to the large number of possible topologically distinct sites a considerable number of geometry optimization runs was necessary.

Figure S1. Amounts of CH_x species generated on $\text{MoC}_{1.1}/\text{Au}(111)$ and $\text{MoC}_{0.6}/\text{Au}(111)$ after several cycles of hydrogen adsorption (1 Torr of H_2 , 300 K, 5 minutes) and desorption (heating at 500 K).



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