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Boosting the activity of transition metal carbides towards methane activation by nanostructuring

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Electronic Supplementary Information

S1 C 1s and Mo 3d XPS data for the carbide nanoparticles.

S2. Additional computational details

S3. Optimized structures for the transition states of CH_4 dissociation on MoC_y/Au(111) models

S4. Optimized structures for the transition states of CH_4 dissociation on δ-MoC or β-Mo_2C surfaces

S1. C 1s and Mo 3d XPS data for the carbide nanoparticles

Figure S1. C 1s spectra collected during the preparation of the $MoC_{1.1}$/Au(111) system. A multilayer of ethylene was adsorbed on the gold substrate at 100 K, 0.3 ML of Mo were vapor-deposited and then the sample was annealed to 750 K to induce the desorption of the excess hydrocarbon and the formation of $MoC_{1.1}$.

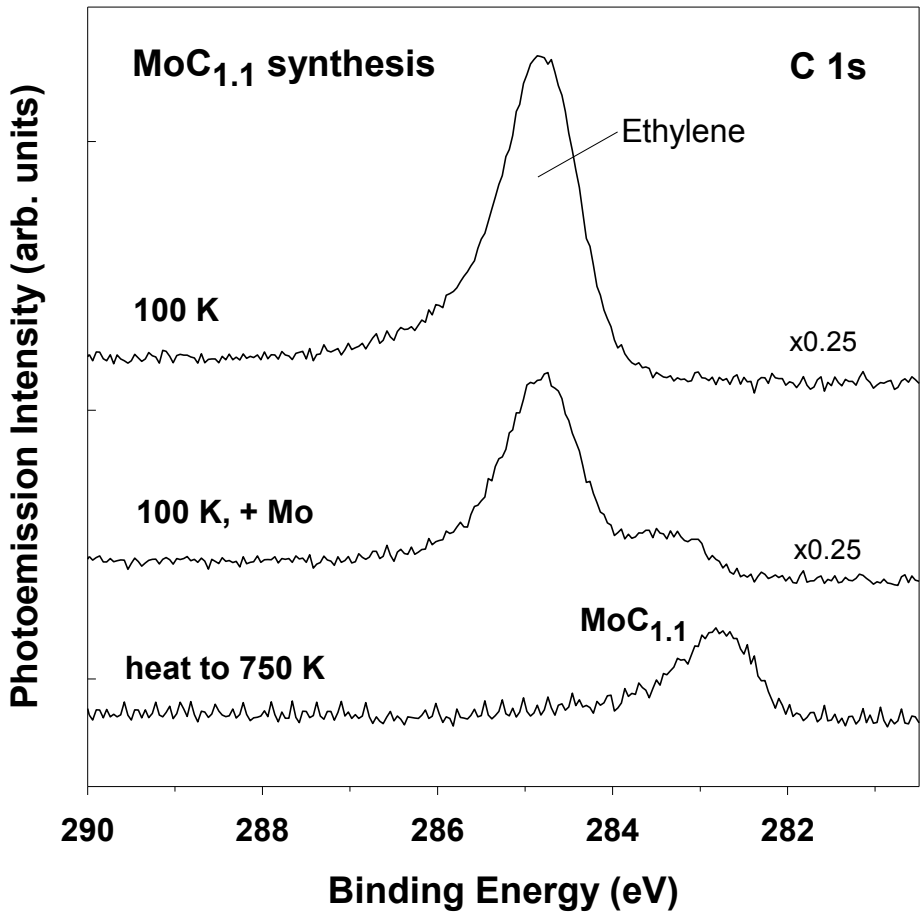
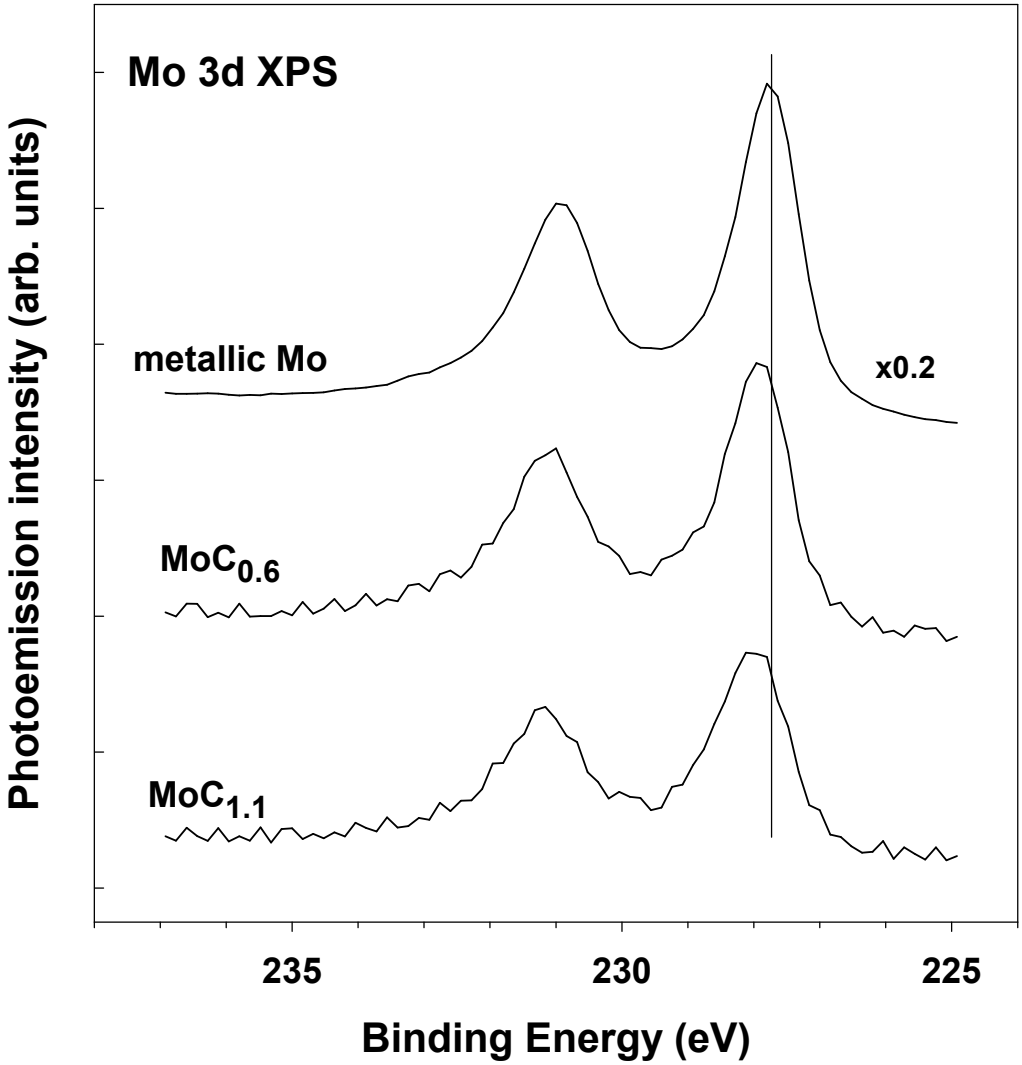


Figure S2. Mo 3d XPS spectra for metallic Mo, $MoC_{0.6}$/Au(111) and $MoC_{1.1}$/Au(111) systems



S2. Computational details

The periodic density functional theory (DFT) calculations have used a valence electron density expanded in a plane wave basis set with a kinetic energy cutoff of 415 eV, chosen to yield total energy variations below 0.01 eV. The effect of core electrons on the valence electron density has been described by the projector augmented wave (PAW) method of Blöchl,[1] as implemented in the VASP code by Kresse and Joubert.[2] The Au(111) surface slab model was built from the pre-optimized bulk unit cell, and contains four atomic layers with the two bottommost fixed as in the bulk to provide an appropriate environment to the fully relaxed two uppermost atomic layers defining the surface region.[3] To avoid interactions between periodic images in the direction perpendicular to the surface, a vacuum region of 30 Å was added. The MoC_y nanoparticles were supported on a (6×6) supercell of Au(111) containing 144 Au atoms, and their structure fully relaxed using a conjugate-gradient algorithm with convergence criteria for electronic and atomic updates of 10^{-5} eV and 0.01 eV·Å^{-1}, respectively. Several initial geometries were tested for each adsorbed MoC_y nanoparticle, and the most stable structure for each size was chosen to study the CH_4 dissociation reaction thereon. 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 orientations of the nanoparticle and the presence of different adsorption sites on the Au(111) surface, a considerable number of geometry optimization runs was necessary.

The δ-MoC(001), and C- and Mo-terminated β-Mo_2C(0001) surface slabs were constructed using the lattice parameter taken from the optimized bulk TMC crystal.[4] The δ-MoC(001) (2√2×2√2)R45º slab contains four atomic layers; the two uppermost ones have been allowed to fully relax, whereas the two bottom layers were fixed at optimized bulk crystal positions to simulate the material bulk. The C- and Mo-terminated β-Mo_2C(0001) slabs contains six atomic; the three uppermost ones have been allowed to fully relax, whereas the three bottom layers were fixed at optimized bulk crystal positions. All surface geometries were optimized before placing any adsorbate. The initial guesses for adsorbate geometries were obtained by placing the adsorbate at different sites. Such optimized geometries were characterized as minima on the potential energy surface by appropriate frequency analysis involving diagonalization of the corresponding block of the Hessian matrix with elements obtained through finite differences of analytic gradients of 0.03 Å length. The necessary numerical integrations in the reciprocal space were carried out using an optimal 3×3×1 **k**-point mesh selected following the Monkhorst-Pack scheme[5] for the MoC_y/Au(111) systems, a 9×9×1 **k**-point mesh for δ-MoC(001), and a 5×5×1 **k**-point mesh for the β-Mo_2C(0001) slabs.

The energy of the isolated gas phase CH_4 molecule was obtained by placing it in an asymmetric periodic box of 9×10×11 Å and considering the Γ-point only. The initial guess for adsorbate geometries was obtained by directly placing the adsorbate at different sites which depends on each chosen system. Methane adsorption energy E_{ads}, was then calculated as:

$$E_{ads} = E_{CH_4/slab} - \left(E_{slab} + E_{CH_4}\right) \quad (1)$$

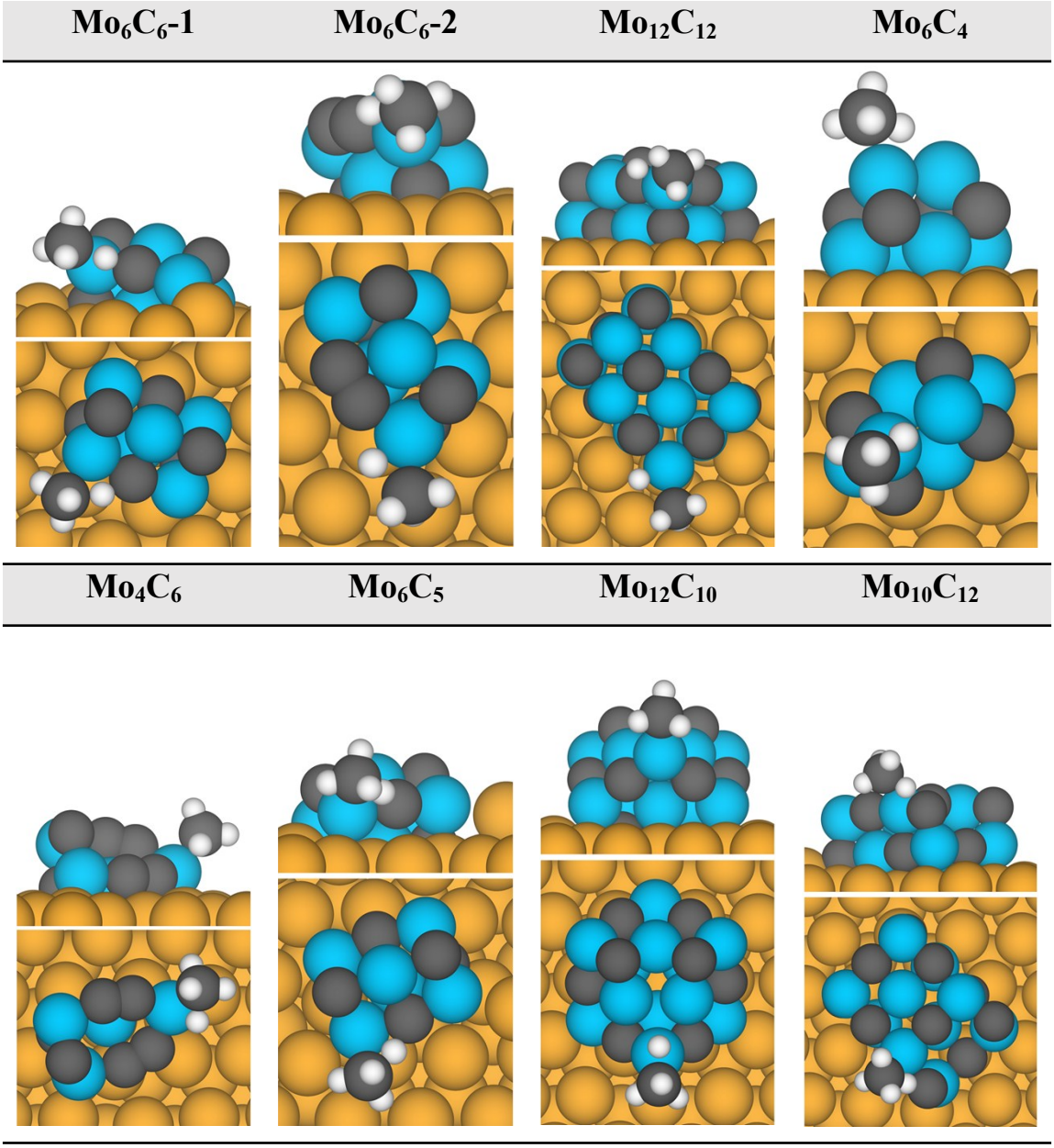
where $E_{CH_4/slab}$ is the energy of the CH_4 species adsorbed on the corresponding slab model, E_{slab} is the energy of the relaxed, pristine slab, and E_{CH_4} the energy of an isolated CH_4 molecule. In the studied MoC_y/Au(111) cases, the slab includes the supported carbide nanoparticle. All energy values include the zero-point energy (ZPE) term, estimated by considering both gas and adsorbed phases, obtained within the harmonic approximation. The reaction energy, E_{reac} has been calculated assuming that the final products are at infinite separation. Hence, it can be calculated from the formation energies of the different adsorbed species (CH_4, CH_3, and H):

$$\Delta E_{reac} = E^f_{CH_3} + E^f_H - E^f_{CH_4} \quad (1),$$

where details on the calculation of formation energies can be found elsewhere.[6]

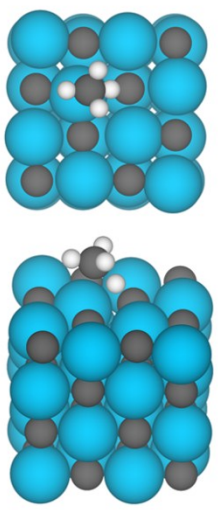
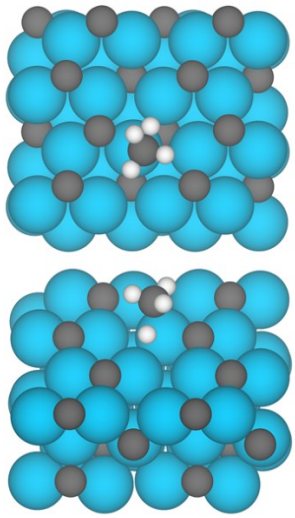
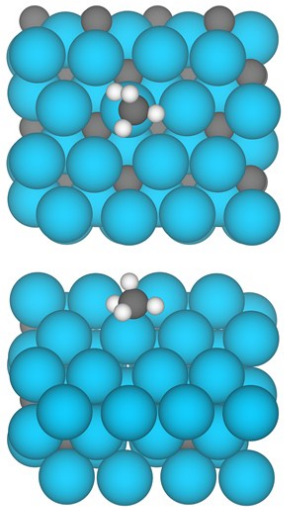
S3. Optimized structures for the transition states of CH_4 dissociation on MoC_y/Au(111) models

Figure S3. Optimized geometries (top and side views) for the transition states of methane first C-H bond scission on all studied MoC_y/Au(111) systems. Colour code as in Figure S1.



S4. Optimized structures for the transition states of CH_4 dissociation on δ-MoC and β-Mo_2C surfaces

Figure S4. Optimized geometries (top and side views) for the transition states of methane activation on δ-MoC(001) and C/Mo-terminated β–Mo_2C(0001) surfaces. Colour code as in Figure S1.

δ-MoC(001)	C-terminated β-Mo_2C(0001)	Mo-terminated β-Mo_2C(0001)
		

References and Notes

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