

FUNDAMENTALS OF METHANOL SYNTHESIS ON MOLYBDENUM CARBIDE BASED CATALYSTS

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CO₂ hydrogenation to methanol and other alcohols constitutes an appealing route to recycle the large amount accumulated in the atmosphere through fossil-derived fuels burning. However, CO₂ high chemical stability makes the overall process difficult and appropriate catalysts are needed. In the current search for new catalysts, transition metal carbides have become an attractive alternative, since they display a catalytic activity for methanol synthesis orders of magnitude higher than commercial Cu/ZnO catalyst.

Here, a theoretical and experimental study has been carried out using (001) surfaces of the cubic δ -MoC and orthorhombic β -Mo₂C, taking into account the two possible terminations (with C or Mo atoms). The CO₂ hydrogenation performed on β -Mo₂C(001) by the experimentalists showed the obtaining of CO, methanol, methane, and other alkanes owing to the high reactivity of the surface, whereas only CO and methanol are obtained using δ -MoC(001) surface.^[1] The experimentalist have demonstrated that these catalysts are potential alternatives for methanol synthesis, in principle dozens of times better than commercial Cu/ZnO based catalysts.^[2]

In order to search the origin of this behavior, a theoretical energy profile has been performed in both surfaces. First of all, the theoretical calculations have shown that β -Mo termination is able to break the CO₂ molecule relatively easy ($E_{\text{act}} = 0.3$ eV), and this step is more favorable than CO₂ hydrogenation so the majority of methanol formation owes to the CO hydrogenation. Furthermore, methane formation ($\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$) needs a prior CO dissociation ($E_{\text{act}} = 1.0$ eV), as determined by experiments, where part of the formed CO is dissociated. Nevertheless, the activation of CO₂ on δ -MoC(001) is low in this surface and E_{act} is superior to the desorption energy. Thereupon, this fact could indicate that the CO₂ hydrogenation is the first step of the synthesis and consequently it implies a different reaction mechanism dependent of the used Mo_nC surface. Moreover, the computational calculations have justified the selectivity of the reaction; the CO dissociation is not happening on on δ -MoC(001) since the E_{act} is 3.0 eV. This fact implies the non formation of atomic C, and the impossibility of methane formation.

[1] S. Posada-Pérez, F. Viñes, P. J. Ramirez, A. B. Vidal, J. A. Rodríguez, and F. Illas, *Phys. Chem. Chem. Phys.* **2014**, 16, 14912.

[2] S. Posada-Perez, F. Viñes, J. A. Rodríguez, and F. Illas, *Top Catal.* **2015**, 58, 159.

