

ZnO ultrathin films on Cu(111) for the catalytic hydrogenation of CO₂ to methanol: STM and XPS study

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Abstract :

The significant increase of carbon dioxide atmospheric concentrations these past decades is one of the major environmental, societal and economical issue the scientific community is facing today. [1,2] Different procedures to stabilize and reduce the global CO₂ atmospheric levels are considered as viable solutions, for instance the reduction of carbon dioxide emissions [3], CO₂ sequestration [3] and CO₂ conversion. [3-5] The chemical conversion of CO₂ to more valuable chemicals has of late received a particularly acute attention from both environmental and economical points of view. Specifically, in the case of the catalytic hydrogenation of CO₂ to methanol, a high commodity chemical which can be used as biofuel for vehicles and as a chemical feedstock for the production of a large range of chemicals including for instance formaldehyde, acetic acid and dimethyl ether.[4, 6] For decades, the state of the art catalysts used for the synthesis of methanol from syngas (CO₂/CO/H₂) constitute of Cu nanoparticles deposited on ZnO and stabilized on a Al₂O₃ matrix and operate at temperatures around 200-300°C and under of pressures around 50 to 100 bar.[6] Although this catalyst has been extensively discussed in the literature, no clear consensus is reached concerning the nature of active sites nor the reaction mechanisms and their key intermediate compounds. Early works in the literature tended to consider metallic copper as active site for hydrogenation and zinc oxide to mainly act as a promoter ensuring spatial dispersity.[7] However, more recent studies emphasize the role of Cu-ZnO sites benefiting from the synergetic effects (structural and electronic) at the metal-oxide interface. [8] Thus numerous experimental and calculation studies further investigated the role of these boundary sites and the hydrogenation mechanism on the simplified model catalyst ZnO/Cu. Although the mechanism is still widely discussed, numerous theoretical and experimental works report mechanisms involving formates [9-12], carbonates [10] and carboxylates [9, 10] as reaction intermediates as well as the importance of the competitive reverse water gas shift reaction. [11] Here we present our first results obtained by a STM and XPS study of ZnO/Cu(111) nanocatalysts after exposition to reactive atmospheres. We present the thickness dependence of both ZnO thin films crystalline structure as well as the influence of thin film morphology on the reaction mechanisms.

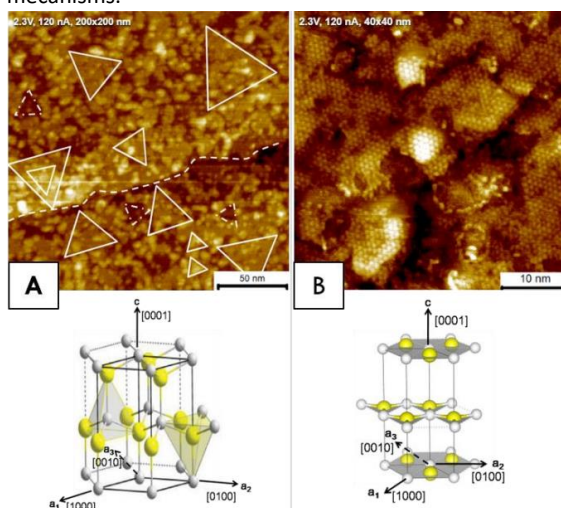


Figure 1 : STM images of ZnO films over [A] and under [B] 4 monolayers thick and their respective crystalline structure models, wurtzite and h-BN). (In [A], the white triangles highlight the preferable growth of ZnO as triangular islands, as expected from the wurtzite structure in UVH.)

References

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