

# CO<sub>2</sub> hydrogenation over ultradispersed Mo/TiO<sub>2</sub> catalysts

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Environmental concerns impose the reduction of CO<sub>2</sub> emissions in the atmosphere. A promising strategy consists in the valorisation of effluent CO<sub>2</sub> through catalytic hydrogenation [1]. In particular, CO<sub>2</sub> can be converted into methanol on the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> syngas-to-methanol catalyst, but the latter is sensitive to water and prone to deactivation. Single-atom or subnanometric cluster-based catalysts are a promising class of materials, which potentially offer maximum atom-efficiency and distinct catalytic properties [2,3]. In this work, we show that Mo ultradispersed on TiO<sub>2</sub> catalyses CO<sub>2</sub> hydrogenation. We focus on the effect of Mo loading and TiO<sub>2</sub> properties on catalyst activity and selectivity to methanol, and on the identification of surface species.

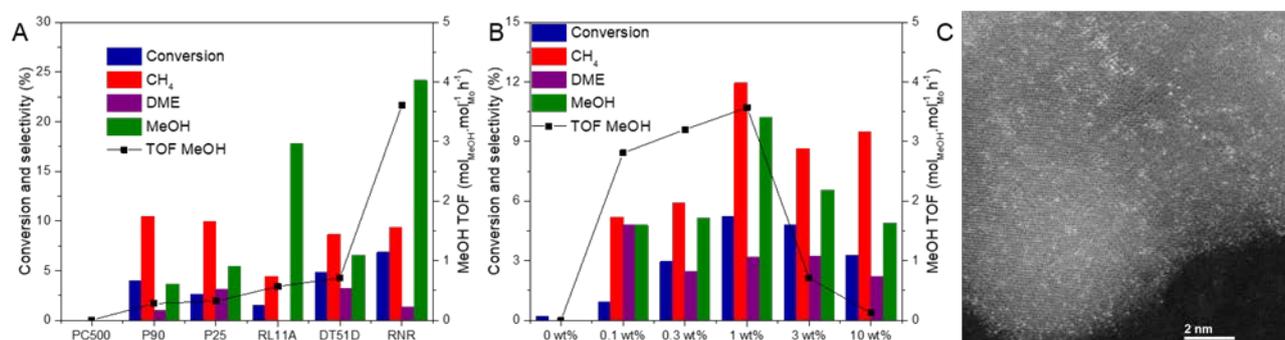


Figure 1: (A,B) CO<sub>2</sub> hydrogenation performances. Effect of support type for 3 wt% Mo/TiO<sub>2</sub> (A) and of Mo loading for Mo/DT51D anatase (B). CO selectivity is not represented. (C) AC-STEM-HAADF image of 3 wt% Mo/DT51D.

Mo/TiO<sub>2</sub> catalysts with 0.1-10 wt% loading were prepared by wet impregnation – reduction using (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> as precursor and homemade rutile TiO<sub>2</sub> nanorods (RNR) together with various commercial forms as supports. The catalysts were characterized by various techniques, including aberration-corrected scanning transmission electron microscopy (AC-STEM), *operando* Raman and X-ray absorption spectroscopies, and near ambient pressure X-ray photoelectron spectroscopy. The catalytic performances were measured using a flow fixed-bed reactor with a H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub> ratio of 3:1:1 at 3 MPa total pressure and 275 °C.

Whereas previous works reported the absence of CO<sub>2</sub> hydrogenation activity of Mo/TiO<sub>2</sub>-P25 [4,5], this work reveals promising performances for selected materials, the most active and methanol-selective catalyst being Mo/RNR (Figure 1A). Carbon monoxide, methane, dimethyl ether and methanol are formed with different selectivities depending on the support. The methanol formation turnover frequency (per Mo atom) greatly increases at lower Mo loadings, i.e. 0.1-1 wt% (Figure 1B). STEM studies (Figure 1C) show that single Mo atoms (oxometallate monomers) replace small clusters (multimers) as the Mo loading decreases, which suggests that isolated MoO<sub>x</sub> species anchored on TiO<sub>2</sub> are the most active ones for methanol production. In this communication, based on several complementary characterization data, we will provide insights on the catalytic performance in relation to the nature of MoO<sub>x</sub> species and the physicochemical properties of the titania surface.

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