



Contribution ID: 50

Type: Flash presentation

MZrO_x (M = Zn, Ga) catalysts for CO₂ hydrogenation reaction: exploiting XAS and PXRD to understand catalyst's structure, activity and stability

Wednesday, 14 September 2022 12:00 (5 minutes)

In the panorama of CO₂ hydrogenation catalysts, the COZMOS project (<https://www.aspire2050.eu/cozmos>) is investigating MZrO_{2-x} (M : Zn,Ga) as potential catalysts for CO₂-to-methanol conversion. Alivalent elements ZrO₂ doping has been largely exploited to improve catalyst's properties through oxygen vacancies (Vo) formation. However, whilst great efforts have been done to improve catalyst performances, very little research investigated how and where the Vo active site was generated during doping. In this contribution, through Powder X-Ray Diffraction (PXRD) and X-Ray Absorption Spectroscopy (XAS) we unveil that two MZrO_{2-x} catalysts having similar catalytic properties are structurally very different. Single phase PXRD patterns are observed for both materials and, as largely accepted, they describe the catalysts as a MZrO_{2-x} solid solutions. Nevertheless, a detailed in-situ - XAS analysis at Zn/Ga/Zr K-edges unveils as: I) ZnZrO_x catalyst consists of ZnO nanoclusters embedded in a ZrO₂ matrix having catalytic active site at the ZnO/VO/ZrO₂ interface and II) Ga substitutionally replaces Zr forming a xGaZr(1-x)/ZrZr(2-x/2)OO solid solution where Ga tetrahedral/octahedral coordination changes under reducing conditions increasing the active sites Ga-VO-Zr concentrations. The different structural nature of the two catalysts drastically affects their reactivity and stability. Indeed, whilst any evident differences are observed for GaZrO_x after reaction, ZnO/ZrO₂ report significant variations of Zn total concentration and local environment. By in-situ PXRD and ex-situ XAS we observe as during H₂ activation ZnO cluster dimension increases favouring Zn sublimation, globally causing a drastic loss of active ZnO/ZrO₂ interface and reducing tetragonal ZrO₂ polymorph stability.

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Session Classification: MS

Track Classification: Understanding Advanced Functional Materials Through Operando Studies