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Operando Raman Spectroscopy Investigations of the CO_2 Hydrogenation to Methanol on Cu-ZrO_2 based Nanocatalysts

The use of catalytic reactions to produce a large variety of valuable chemicals is a crucial process in the catalysis industry. In particular, the synthesis of methanol (CH_3OH) from the catalytic CO_2 hydrogenation reaction (CO_2 HR), $(CO_2 + 3H_2 \rightarrow CH_3OH + H_2O)$, has grown tremendously within the last few years, as it is an attractive approach to mitigate CO_2 by converting it into high value-added chemicals.
Within this framework we have conducted a comparative study of the CO_2 hydrogenation on two analogues nanocatalysts, the first in the form of mixed nanopowders of Cu-ZrO_2-ZnO-Al_2O_3 (CZZA), and the second consisting of ultrathin film of ZrO_2 grown on CuOx/Cu(111) surface. This comparative approach is intended to unravel the reaction mechanistic of the CO_2 HR. To this end, we have conducted operando Raman spectroscopy measurements using autoclave cells under realistic reaction conditions of the pressure (10-40 bar) and step-wise annealing from room temperature up to 400°C. Our study shows two major findings. The first concerns the reaction path followed during the CO_2 hydrogenation to methanol. It occurs via the reverse water gas shift mechanism (r-WGS). We have used isotopic labeling (D_2) to monitor the formation of D_2O specifically through the r-WGS process. Raman band shift of D_2O and other relevant intermediates such as CO, HDO were detected in the gas phase (Fig.). The second finding shows high catalytic performances of the ZrO_2/CuO_x/Cu(111) ultrathin film compared to the CZZA nanopowders. It is illustrated by the early onset of the r-WGS process which occurs at 100°C on the ZrO_2 films while it starts only at 200°C on the CZZA sample. Besides, the CO_2 conversion via the r-WGS is more efficient on the ZrO_2 films as it produces large amount of D_2O for less consumption of D_2 when compared to the CZZA sample. We attribute the better performances of the ZrO_2 ultrathin films to following effects: (i) the ZrO_2—CuOx/Cu interface where synergistic phenomena occur (CO_2 dissociation on ZrO_2 and D_2 dissociation on CuO_x), (ii) the unique role of the dual-reaction sites of ZrO_2, present in the ultrathin film, that are the strong Lewis acidity of Zr^{4+} cations and the strong Lewis basicity of both O^{2-} anions and oxygen vacancies (O_v) associated with Zr^{3+} states. We have evidenced the presence of these sites thanks to XPS investigations conducted on the ZrO_2 ultrathin films where the core-level spectra in the Zr binding energy region show the presence of two contributions, Zr^{4+} and Zr^{3+}.

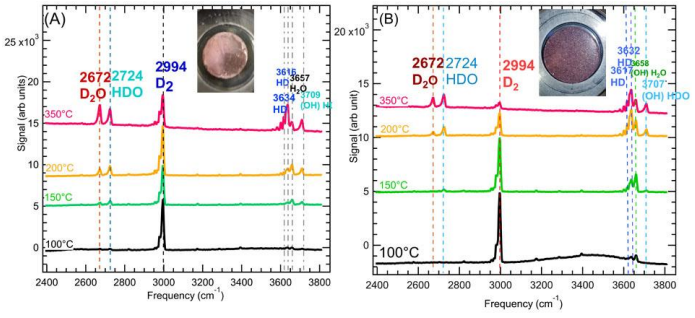

Figure: Operando Raman spectra as a function of the temperature for two nanocatalysts. (A): ultrathin film of ZrO_2 grown on CuOx/Cu(111) surface; (B) nanopowders of Cu-ZrO2-ZnO-Al2O3 (CZZA)