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Towards the understanding of the direct methane to methanol reaction mechanism catalyzed by CeO_2/Cu_xO nanomaterial: an operando NEXAFS study

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Nowadays the direct methane to methanol (DMTM) reaction is considered as the "dream reaction", because it allows to convert in one step CH_4 (a greenhouse gas) to a very useful chemical feedstock and portable fuel such as methanol (CH_3OH), avoiding the over-oxidation to CO_2. The research for a successful catalyst/oxidant combination which is able to provide good methanol selectivity at a reasonable methane conversion is particularly challenging. One emerging system is the so called "inverse" catalyst CeO_2/Cu_2O, that has demonstrated CH_4 conversion to methanol with high selectivity [1]. In this system, the interaction between CeO_2 and Cu_2O seems to have a key role, however the reaction mechanism is still not well understood. In this study we investigated two CeO_2/CuO based systems, obtained with different synthesis methods: the first material was synthetized through pulsed laser deposition (PLD) [3] in order to obtain a model system similar to the one previously reported [1], while a second sample was prepared through a more scalable milling process. In order to address the fundamental aspects of the DMTM reaction mechanism on these systems, a soft X-Ray *operando* NEXAFS study was performed. This technique provides a very high sensitivity to the local chemical environment of the active species involved in the reaction. This kind of operando experiment at 1 bar is possible only with the proper setup that is available at the APE-HE beamline of the Elettra Synchrotron Radiation source (Trieste) [2]. The spectral evolution of Ce $M_{4,5}$ and Cu $L_{2,3}$ absorption edges of the catalysts were followed during the reaction, under experimental conditions similar to those reported in [1]. At the same time, the gas products were detected through an online micro-GC. The operando NEXAFS spectra confirmed that CH_4 interacts strongly with the sample at 250°C, showing a progressive Cu reduction during the exposure to methane. Gas chromatographic analysis showed, in addition to CO/CO_2, the production of CH_3OH and CH_2O. The comparison of the results of NEXAFS experiments for the model and polycrystalline catalyst shed light on new aspects of the role of the CeO_2/Cu_2O catalyst in promoting the DMTM reaction.

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