Methanol Synthesis Pathways for the Selective Conversion of C-H bonds

Sanjaya D. Senanayake,
Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973 (USA)

Methane remains a valuable yet underutilized resource, with great interest for the direct upgrade to valued products. Our recent studies indicate that, in spite of the high stability of methane, systems such as Ni-CeO_2(111) and CeO_2-Cu(111) can break C-H bonds even at room temperature, through careful manipulation of interfaces and metal-support interactions, using light oxidants (CO_2, O_2/H_2O). the selective oxidation on the surface sites can lead to conversion steps that produce CH_3OH and CO+H_2. AP-XPS with the help of DFT has been essential to elucidate C-H activation and oxidation steps with high resolution C 1s and O 1s spectroscopies.

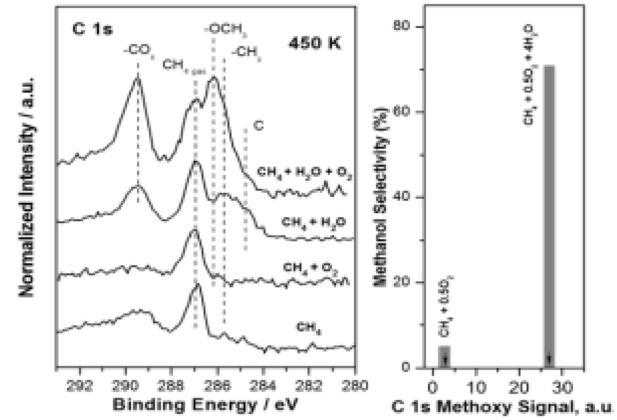

Figure 1. a) C 1s AP-XPS spectra when exposing a CeO2/-Cu2O/-Cu(111) surface (θCeO2~ 0.5 ML) to different gas reactants at 450 K. b) Methanol selectivity versus the amount of methoxy generated with and without adding addition of water to sequence the steps that can produce methanol directly from methane.

We have established a method for the direct conversion of methane to methanol building on these surface results yielding low methanol selectivity (~30%). Subsequently, and in remarkable contrast we have found that a CeO_2/Cu_2O/Cu(111) inverse system is able to activate methane at room temperature and then, with the help of water, performs a highly selective (70%) catalytic cycle, for the production of methanol. The interfacial interaction between CeOx-CuOx is crucial while the concentration of water has a strong effect on the selectivity towards the production of methanol.

We have used AP-XPS to track the sequence of pathways that initially activate C-H bonds into -OCH3 surface species that leads to the production of methanol. DFT and KMC were then used to evaluate the most prevalent steps that are likely essential for such selective chemistry.

This work is funded by the U.S. Department of Energy under contract No. DE-SC0012704. XPS measurements were performed at beamline 9.3.2 at the Advanced Light Source of LBNL under contract no. DE-AC02-05CH11231.

1. Liu et al. Science (2020) 368 (6490), 513-517
2. Liu et al. Angewandte Chemie (2016) 128 (26), 7581-7585.
3. Lustemberg et al. ACS Catalysis (2016) 6 (12), 8184-8191.
4. Zuo et al. JACS (2016) 138 (42), 13810-13813.
5. Liu et al. Angewandte Chemie (2017) 56 (42) 13041-13046.
6. Zhang et al. ACS Catalysis (2018) 8 (4), 3550–3560.
7. Lustemberg et al. JACS (2018) 140 (24), 7681–7687.
8. Liu et al. ACS Catalysis (2019) 94 3349-3359.
9. Zhang et al. J. Phys. Chem. (2019) 122 (50), 28739-28747.