From carbon dioxide to methanol: the nanomaterials opportunities.

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February 2024

The concentration of CO_2 in the atmosphere has been increasing steadily since the first industrial revolution in the 18th century, with a more and more rapid evolution in recent years. It is undeniable that this increase in concentration comes from human activity and the 35,000 Mt of anthropogenic CO_2 released into the atmosphere yearly. By itself, the carbon dioxide is responsible for 45% of the greenhouse gas effect, thus, the carbon capture and utilization is a key strategy to tackle global warming. The obtention of a valuable green fuel and platform molecule such as methanol from this greenhouse gas can pave the way to a more sustainable future by following the "methanol economy" concept. The methanol synthesis from CO_2 can be achieved using electro-, bio-, photo- or thermal catalysis with appropriate catalysts.

In this talk, after presenting a quick introduction on different CO_2 utilization processes, the CO_2 hydrogenation to methanol over Mo/TiO_2 single-atom catalysts and the CO_2 photoreduction to methanol over waste-derived carbon nanodots will be detailed.

For the CO_2 hydrogenation to methanol, beyond the industrial $Cu/ZnO/Al_2O_3$ syngas-to-methanol catalyst, alternative materials have been suggested to enhance both the methanol yield and the catalyst stability. However, these catalysts often rely on rare and/or strategic elements such as Au, Pd, In, Ga, Zn, and Ce. Therefore, the elaboration of a novel, green, non-critical and cost-effective alternative is desirable. Previously described as inactive, the Mo/TiO_2 system was recently revealed efficient for CO_2 hydrogenation to methanol. It appeared that the reaction kinetics strongly depends on the titania phase, rutile nanorods (RNRs) exhibiting the best performance. Moreover, the potential of molybdenum ultradispersed on other transition metal oxides, such as CeO_2, ZnO, Al_2O_3, and ZrO_2 for methanol synthesis from CO_2. In the (most promising) case of titania, an in-depth operando X-ray absorption spectroscopy (XAS) investigation was carried out to decipher the nature of the active phase.

Concerning the photoreduction approach, the sunlight-driven photocatalytic process has the advantage to be both environmentally and economically friendly without requiring any additional energy. Various catalytic systems based on metals including noble metals have been proposed but only low selectivity and conversion are reached. Thus, efficient materials need to be design for this application. The 2023 Nobel Prize in Chemistry was awarded to Moungi Bawendi, Louis Brus, and Aleksey Yekimov for their discovery and synthesis of quantum dots, which are zero-dimensional nanoparticles with dimensions below 10 nm. In particular, the carbon nanodots have attracted significant research attention due to their enviable properties, such as water solubility, desirable fluorescent behavior, ease of functionalization, low toxicity, and biocompatibility. Following the Green Chemistry principles, these materials can be obtained from biomass waste, ensuring tailored properties that make them valuable in several fields such as drug delivery, bioimaging, sensing, water remediation, and photocatalysis. In this part of the talk, the design of metal-free and dopant-free biomass/waste-derived carbon nanodots for methanol-selective CO_2 photoreduction will be discussed.