CO_2 conversion by subnanometer clusters: Control of selectivity by cluster size, composition and support

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Significance and Relevance

In this paper we address a high-level control of activity and selectivity achieved *via* the size- and atomic composition of subnanometer Cu and CuPd clusters along with the composition and morphology of the support, allowing to switch between products methanol. methane, carbon monoxide and C2 hydrocarbons.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling; CO2 utilization and recycling
Preferred presentation: Oral only

Introduction and Motivations

The study focuses on the gas-phase catalytic conversion of carbon dioxide[1] with hydrogen, under mild pressure and temperature conditions, with the goal to identify efficient catalysts with their performance tunable between various products such as methanol, methane, carbon monoxide and hydrocarbons.

Materials and Methods

As catalytic active centers, small monometallic clusters of copper consisting of a handful of atoms (between 3 and 20 atoms) were used, generated ligand-free in a magnetron sputtering source and after mass selection of size with atomic precision deposited on supports made of amorphous alumina and iron oxide, as well as amorphous and nanocrystalline zirconia. The thin, 3 monolayer to 1 nm amorphous supports films were prepared by atomic layer deposition, the nanocrystalline zirconia one in molecular beams. The catalysts were then tested under 1.1 atm pressure, with CO_2 and hydrogen seeded in He.

Results and Discussion

Copper clusters of three sizes, with 3, 4 and 20 deposited on alumina film were investigated, revealing Cu4 clusters with the highest activity in producing methanol at 250 °C[2,3] (Fig 1a) as the only product at a rate of $4x10^{-1}$ methanol molecules produced per deposited copper atom and second.

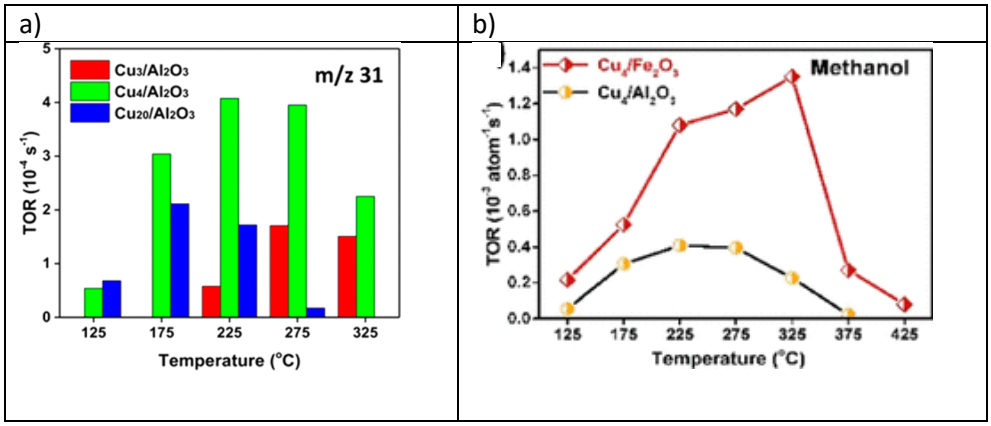

Figure 1 (a) Cu cluster size-dependent activity in methanol formation; (b) increase of methanol formation for Cu4 clusters supported on iron oxide, (c) .

Next, the effect support on catalytic performance of clusters was studied. When using iron oxide as the support for Cu_4 clusters[4], thanks the symbiotic interplay between the two metal components, the catalysts selectivity with temperature shifted between the formation of methanol (Fig1b and C2 hydrocarbons, while boosting methanol production 4-fold in comparison with the alumina support).

To further leverage the effect of the support and its morphology on performance, the studies continued with Cu_4 and Cu_{12} clusters supported on amorphous alumina and nanocrystalline zirconia[5], with selectivity switched fully to the formation of methane peaking at 375 °C. Cluster supported on nanocrystalline zirconia showcased a 2-fold increase in activity, confirming the role of surface morphology (i.e. bod length and structure) on the performance of the clusters, presumably via altered structure of clusters due their epitaxial wetting of the surface.

The aforementioned results demonstrate the available controls in efficient CO_2 conversion, of both activity and selectivity, by cluster size and cluster-surface interactions. For the conclusion of the paper, recent results on further optimizing the process of CO2 conversion on subnanometer clusters, results obtained by utilizing and additional tuning know, extension to bimetallic clusters of CuPd will be presented, changing the composition of 4- and 5-atom CuPd clusters one atom a time, following predictions from theory.[6]

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