Karlsruher Institut für Technologie

Institut für Technische Chemie und Polymerchemie (ITCP)

Masterarbeit

Photo-enhanced CO_2 hydrogenation over diluted alloy catalysts based on Ag plasmonic nanoparticles

Study program

Work oriented to students from the chemistry and chemical engineering faculties.

Take part in a small, young, motivated and international group.

Start

Earliest May 2025

Contact person

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Motivation

CO_2 hydrogenation, a key reaction within the green economy paradigm, has gained increasing attention in the last decade as it would be an alternative to the current fossil fuel-based production of platform molecules (i.e. methanol, methane, CO, fuels), driving their synthesis towards a more sustainable process. Different catalysts have been developed and studied based on a range of transition metals, from where scaling relationships and volcano-type curves as a function of a particular reaction descriptor have been established.

Scalling correlations based on Brønsted-Evans-Polayni (BEP) relationships state that the energy of a particular reaction scales linearly with its activation energy. In other words, both parameters can be correlated, resulting in volcano plots (Figure 1), from where the Sabatier principle is stated: the optimum catalyst is the one that does not bind intermediates too strongly nor too weakly. These correlations are well understood for thermocatalytic CO_2 hydrogenation over a range of transition metals. Different studies and research groups are advocated on paths to break these scalling relationships and, therefore, improve catalysts. One alternative is diluted alloys between a host coinage metal (e.g. Cu, Ag, Au) and a minoritary transition metal (e.g. Rh, Pt, Pd, Ru, Fe, Ni), down to the scale of single atoms, therefore providing a distinct active site for the reaction under study. Moreover, the coinage metals are able to be excited by light due to their plasmonic nature, which represents an additional source of energy to drive chemical transformations and to escape scalling relationships. Although an attractive topic, volcano plots over diluted alloys for CO_2 hydrogenation under visible light illumination remain unstudied.

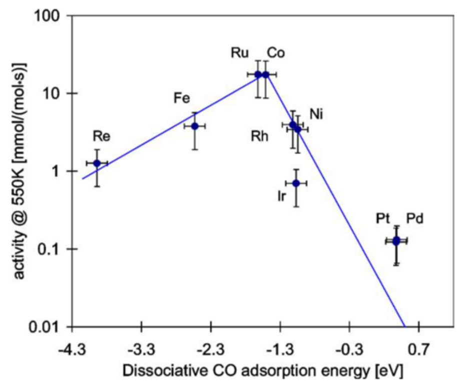

Figure 1. Volcano plot for dissociative CO adsorption. Figure reproduced with the permission from [1]. Copyright Elsevier 2024.

In this sense, the objective of this study is to set the foundations for the understanding of scaling relationships under visible light over a series of Ag-based plasmonic diluted alloy catalysts. The work is purely experimental and consists on the characterization of the materials within two main dimensions: surface structure and kinetics. The former will be tackled by employing CO as a probe molecule in combination with FTIR-spectroscopy. On the other hand, in depth kinetic measurements under visible-light will be performed to understand the involvement of LSPR in CO_2 hydrogenation and its relation with the structure of the catalysts. Therefore, the work is higly interdisciplinary, as it resides at the interface between surface science and chemical reaction engineering. Additional *ex situ* and *in situ* characterization techniques will be performed to shed further light onto the structure of the catalysts.

For further information and queries, do not hesitate to contact Dr. Arik Beck (arik.beck@kit.edu).

[1] Bligaard, T., Nørskov, J. K., Dahl, S., Matthiesen, J., Christensen, C. H., & Sehested, J. (2004). The Brønsted–Evans–Polanyi relation and the volcano curve in heterogeneous catalysis. *Journal of catalysis*, *224*(1), 206-217.