

Laterally Condensed Catalysts for Hydrogenation Reaction

Katarzyna Skorupska¹, Zehua Li¹, Eylül Öztuna^{1,3}, Christian Rohner¹, Alexander Steigert², Olga V. Vinogradova¹, Afshan Jamshaid¹, Thomas Götsch¹, Zahra Gheisari¹, Frank Giergsdies¹, Daniel Cruz¹, Sabine Wrabetz¹, Jutta Kröhnert¹, Shan Jiang¹, Daniel Delgado¹, Martin Muske², Tobias Köchler², Wiebke Frandsen¹, Adnan Hammud¹, Olaf Timpe¹, Annette Trunschke¹, Thomas Lunkenbein¹, Daniel Amkreutz², Helmut Kühlenbeck¹, Vanessa J. Bukas¹, Axel Knop-Gericke^{1,5}, Iryna Antonyshyn^{1,4}, Rutger Schlatmann², Karsten Reuter¹, Robert Schlögl¹, Beatriz Roldan Cuenya¹,

¹ Fritz-Haber Institute of the Max Planck Society, Berlin, Germany

² PVcomB, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

³ Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

⁴ Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany

⁵ Max Planck Institute for Chemical Energy Conversion, Mülheim, Germany

The selective hydrogenation of acetylene to ethylene holds significant industrial relevance. Acetylene, along with black carbon, is produced in pyrolysis processes that are utilized to protect hydrogen from CO₂ hydrogenation products. Due to safety concerns, it is imperative to selectively hydrogenate acetylene from the product stream into valuable ethylene. In this study, a 2-D catalyst concept—laterally condensed Pd and Pd-Au catalysts (LCC)—was used to investigate the formation and development of the catalyst during the acetylene hydrogenation reaction. The characterization of the multidimensional processes controlling catalyst selectivity, including electronic and geometric effects, necessitates model and functional system in one like LCC. Thin film technology available from photovoltaics was used to obtain the well-defined LCC catalyst geometry. A few nanometers thick Pd and Pd-Au LCCs with dual interfaces—one functional non-reactive with the support, and the other reactive with the reaction gas feed—were evaluated through prolonged time-on-stream catalytic measurements. Prolonged operation (>20 h) revealed that superior initial selectivity for the Pd-Au catalysts is lost at later times due to significant Pd segregation; an effect not accounted by DFT calculations. We demonstrate that in Pd-Au LCC, Au temporarily acts like atomic carbon (Pd:C) in interface of Pd LCC, influencing the local electronic properties of the Pd (DFT) catalyst and altering the mesoscopic population of subsurface species. This interaction leads to an increase in selectivity for the desired ethylene by lowering the binding energy of acetylene and ethylene, while keeping atomic hydrogen (Pd:H) away from the surface. Additionally in presence of Au the isolated Pd sites were found that are that are known to increase the selectivity to ethylene. However, the segregation of more active Pd to the surface as observed on the mesoscopic scale eventually renders Au obsolete. On the macroscopic scale less blocking carbon was observed on the PdAu LCC surface. Additionally, Au added to Pd LCC mitigates catalyst agglomeration, which appears not to influence the selectivity of the process. Also, single-phase bulk catalysts with different atomic ratios of Pd to Au were studied as reference catalysts.