Consequence of Alloying and metal-oxide interface in bimetallic PtGa Propane Dehydrogenation catalysts prepared via Surface Organometallic Chemistry on Carbon

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The non-oxidative propane dehydrogenation (PDH) reaction has become an intense field of research in both academia and industry, due to the increase in demand of propylene combined with the emergence of shale gas as a major chemical feedstock.[1] Due to its industrial relevance, numerous supported Pt-based bi- and multi-metallic model systems have been investigated with the goal to understand the effect of promoters.[2] In recent years, surface organometallic chemistry (SOMC) combined with thermolytic molecular precursor (TMP) approach has proved to be a powerful tool to prepare tailored, highly active and well-defined silica-supported bimetallic PDH catalysts based on PtGa[3], PtZn[4], as well as PtMn[5] nanoparticles. In these Pt-based systems, the major role of the promoters was attributed to the formation of alloyed nanoparticles, resulting in Pt-site isolation, improved propene selectivity and increased stability against coking. However, the effect of the oxide support, is typically disregarded, since it is considered to be inert to the reaction conditions.

In this work, we make use of the SOMC/TMP approach to investigate PtGa-based PDH catalysts on carbons with the goal to better understand the effect of Ga as a dopant and the role of the nanoparticle-oxide interface on the catalytic performance. The decomposition of the ligand sphere of the grafted precursors, allows for the tailored introduction of an oxide interface, which enables to study interfacial effects of oxide interfaces on the catalytic performance in the PDH reaction.

We show, that alloyed, bimetallic PtGa nanoparticles supported on carbon can be generated via this methodology with almost identical spectroscopical features and catalytic properties as observed for SiO_2 supported analogues.[3] We were able to show that thus prepared carbon-supported, monometallic platinum nanoparticles are highly crystalline. In contrast, bimetallic PtGa particles were found to be less crystalline or even amorphous. These results further consolidate the role of Ga in Pt site-isolation and in enhancing of the surface atom mobility. Additionally, while not necessary for the stabilization of the nanoparticles against sintering, the presence of an oxide interface was found to promote the rate of reaction.

Overall, the strategy for the preparation of tailored bimetallic materials on carbon offers a platform for the preparation and study of interface and dopant effects in thermal catalysis, and can be readily extended to electrochemical applications.

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