

## **New Horizons for Heterogeneously Catalyzed CO Insertion Reactions: From Molecular Sieves to Extended Complex Solids**

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Since their discovery the two most important homogeneously catalyzed carbonylation reactions namely carbonylation of methanol to acetic acid and the hydroformylation of olefins to aldehydes have become important and unrivalled large-scale industrial processes. In the early years of development, cobalt carbonyl complexes played a large role in both catalytic processes. Today cobalt is still used as catalysts for mid- and long-chain olefins, whereas for the short-chain olefins like ethylene and propylene cobalt catalysts were quickly replaced by inherently more active and selective rhodium complexes modified with phosphine or phosphite ligands, for the manufacture of acetic acid today iridium and rhodium based catalyst systems with inorganic modifiers play the largest role [1].

Challenging with using the distinctly more expensive noble metal in a homogeneously catalyzed process is an effective separation of the catalyst from the reaction products. This explains why great care is taken for the separation of rhodium in the hydroformylation of low-boiling compounds where an economic distillative separation is possible at all, or alternatively the process is run biphasic keeping the catalyst in one phase. However, since rhodium losses have to be avoided even in the ppm range great care has to be taken in order to minimize the risk of rhodium loss. The very same considerations are true for iridium and rhodium in the manufacture of acetic acid, although here also great care has to be taken as highly corrosive iodine is employed as co-catalyst.

Technical solutions involving heterogeneous catalysis in both, the hydroformylation of small olefins and the carbonylation of methanol with the catalyst in the solid phase and the products in the gas or liquid phase could offer interesting alternatives which could also lead to new solutions with regard to process design.

In 2006 Iglesia and co-workers reported for the first time a feasible approach for the gas-phase carbonylation of methanol using a heterogeneous catalyst [2]. The material of choice was identified as zeolite catalyst. Today it is well understood on a mechanistic level how a zeolite can catalyze the carbonylation reaction and which role dimethylether plays a critical intermediate in the reaction.

Similar research activities in academia and industry were focused on the synthesis and development of truly heterogeneous or heterogenized molecular hydroformylation catalysts (e.g. SILP process [3]) which proved to be inferior compared to the current state of the art in homogenous catalysis.

Platinum group metal phosphides are known to be useful heterogeneous catalysts and have been applied since years in academia especially for hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO) reactions [4]. Although phosphides show high catalytic activity in different reactions they have never been considered as candidates for the hydroformylation of lower olefins. Herein, we want to show the usefulness of supported platinum metal phosphide catalysts for the hydroformylation of ethylene and propylene as highly active, selective and durable catalysts [5].

In the presentation we will compare similarities and differences between homogeneous and heterogeneous pathways in catalysis for CO-insertion reactions based on the current understanding of the catalyst systems.

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