**The dream becomes a reality: Evonik and LIKAT achieve breakthrough in "Dream Reaction" in carbonylation chemistry**

When producing fine chemicals on a large scale, the cost factor is a decisive point and the demand for cost-effective and efficient synthesis processes is correspondingly high. The optimization of chemical reactions and industrial processes with the help of catalysis as a key technology, enables a more sustainable use of raw materials and energy sources as well as loss-free utilization of the starting materials. A tailor-made catalyst accelerates the reaction, prevents the formation of by-products and thus reduces the energy requirement of the entire process.

Carbonylation reactions are among the most important applications of industrial catalysis. The catalyzed introduction of the CO group takes place through the use of carbon monoxide (CO), which as an important C1 building block in the chemical industry can be obtained both from fossil resources (coal, gas) and from renewable sources (CO2 or biowaste). Carbonyl compounds (aldehydes, acids, esters) are produced annually on a scale of several million tonnes and are used for numerous consumer goods.

Despite the first discovery of homogeneously catalyzed carbonylation processes almost eighty years ago, challenges remain unsolved, above all the direct dicarbonylation of 1,3-dienes. This so-called "dream reaction" would enable a more environmentally friendly, atom-economical production of adipate diesters. These compounds are building blocks of polyamides and polyesters which are produced on a large scale. In particular, adipate diesters are used in plasticizers, perfumes, lubricants, solvents, various pharmaceutical active ingredients and, in terms of quantity, mainly for the production of nylon.

Currently, adipate diesters are produced industrially by oxidising a mixture of cyclohexanol and cyclohexanone with an excess of nitric acid, followed by esterification with the corresponding alcohols. This process requires special equipment due to the corrosive effect of the acid. In addition, stoichiometric amounts of nitrous oxide (N2O) are released, which while binding stratospheric ozone, is 300 times more harmful than CO2 as a greenhouse gas.

This makes the work of the LIKAT scientists (Prof. Dr. Matthias Beller, Dr. Ralf Jackstell, Dr. Helfried Neumann, Jiawang Liu, JiYang) in cooperation with Prof. Dr. Robert Franke, Evonik Performance Materials GmbH and Associate Professor of Chemistry at the Ruhr University Bochum all the more impressive and significant. They developed a palladium catalyst with a specially designed pyridyl functionalized bisphosphine ligand that enables the highly selective and efficient double alkoxy carbonylation of 1,3-butadiene to adipic acid esters in one step.

The key to success was the ligand design. The combination of a bidentate phosphine ligand with a basic pyridyl substituent on the phosphorus and a palladium precursor provides dialkyl adipates in the dicarbonylation of 1,3-butadiene in a ≥95% yield and with ≥97% selectivity.

The difficulty lies in the complexity of the dicarbonylation reaction, which as a rule tends to form numerous by-products (Fig. 1). The simultaneous introduction of two CO groups poses several challenges in this catalytic process: (i) The simultaneous creation of two different carbonylation reactions on a diene substrate (which no other working group had succeeded in doing before); (ii) The selective formation of the linear dicarbonylation product, despite the fact that the isomerization of the originally formed monocarbonylated intermediate to the terminal olefin is thermodynamically particularly unfavorable; (iii) the suppression of other secondary reactions such as telomerisation, hydroalkoxylation and (co)polymerisation.



Fig. 1: Complex network of reactions involved in the synthesis of adipatic diesters from 1,3-butadiene, carbon monoxide and alcohol.

In the development of a suitable catalyst, palladium-coordinated, base modified derivatives of the 1,2-bis [(di-tert-butylphosphino) methyl] benzene ligand (L1, dtbpx), which is used for the large-scale production of methyl methacrylate, were selected as the catalyst of choice. Initial optimization studies with this ligand showed low activity but good selectivity (Table 1). The installation of suitable basic groups leads to a significant increase in activity. However, as the direct comparison between L1 and the dual base-modified L4 shows, this is at the expense of selectivity. The solution was to combine the two structural elements. The specially developed L5 (HeMaRaphos) combines the excellent selectivity of L1 and the high reactivity of L4.



Table 1: Comparison of the different phosphine ligands with regard to reactivity and selectivity.

Through supplementary studies on the performance and optimization of the catalyst system, the direct double carbonylation of 1,3-butadiene to adipate diesters with high catalyst sales figures (> 60,000), high yields (up to 95%) and outstanding selectivity (> 97%) is now possible. The catalyst system can also be transferred to other dienes, paving the way for a revolutionary synthesis process for many fine chemical productions.

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**C4-chemicals@evonik.com**

**www.evonik.com/C4chemicals**