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Catalysis for Fine Chemicals – Symposium in Basel Showed New Applications

After former meetings in Poitiers/France, the '4th International Symposium on Heterogeneous Catalysis and Fine Chemicals' was held for the first time in Switzerland's chemistry metropole Basel from September 8–12, 1996. 270 Scientists attended the meeting, more than a third of them came from industry – reflecting the importance of catalysis as practical science.

The program consisted of 4 plenary lectures, 28 oral contributions and ca. 90 posters, all together covering a broad range of reactions and aspects such as: oxidations, hydrogenations, alkylations, acylations, isomerizations, new types of catalysts, new fine chemical processes, chemical engineering, and even modelling.

Interestingly, the congress started with a review over present use and future potential of homogeneous catalysis. *M. Beller* (München) predicted future fine chemical processes using palladium-catalyzed reactions, asymmetric catalysis, and two-phase catalysis. The possibilities and drawbacks of the two cultures in catalysis, heterogeneous and homogeneous reactions for the synthesis of fine chemicals, were beautifully described in the lectures of *U. Beutler* (Sandoz) and *P. Baumeister* (Ciba). While *Beutler* and coworkers presented a new process for terbinafine, an antimycotic agent which is actually produced by a homogeneous palladium-catalyzed coupling reaction as key step, *Baumeister* and coworkers showed the economic importance of multiple use of palladium both in a homogeneous *Heck* reaction and a consecutive heterogeneous hydrogenation for a herbicide intermediate. Another example for a new industrial fine chemical process came from two of the organizers themselves. Clearly, a highlight of the conference was the joint lecture of *R. Bader* and *H.-U. Blaser* (Ciba), who presented the case history of a process for the agrochemical Metolachlor. The critical

step in the synthesis is a hydrogenation of an imine. Based on nearly twelve years of research, an excellent catalytic asymmetric hydrogenation method using chiral iridium-phosphane complexes was developed. The new process has impressive characteristics and sets a standard for the enantioselective hydrogenation of imines. Optical yields of ca. 80% and catalyst turnovers > 1 000 000 were achieved.

Besides new industrial applications of catalysis, ways of heterogenization constituted a major topic of the symposium. In this regard, a number of new catalysts – for a large variety of reactions – has been prepared by anchoring, grafting, or immobilization. Convincingly, *P.A. Jacobs*' (Leuven) plenary lecture dealt with ship in the bottle catalysts for selective oxidations in liquid phase: dinuclear manganese complexes encapsulated in zeolites are efficient epoxidation catalysts, show suppressed catalase and allyl oxidation activity and are more stable against self-oxidation than their homogeneous counterparts. Fixation of the catalysts in elastomeric membranes (PDMS) results in catalytic membranes, designed for use in solvent-free reactions. Another example for heterogenization came from industry and was given by *S. Wieland* and *P. Panster* (Degussa AG): they use polysiloxanes bearing alkylsulfonic acids as commercial, structurally stable, and noncorrosive substitutes of liquid acids in a variety of acid-catalyzed reactions with high selectivities and activities. Furthermore, these materials can be used as supports for metals, resulting in bifunctional catalysts.

A completely different approach to supported catalysts was followed by *A. Choplin et al.* (Villeurbanne). They designed isolated, stable eight-electron zirconium species on silica to yield catalysts for alkane activation, reductions, and oxidations. Activities of the systems are quite good and recycling is currently under in-

vestigation. Zeolites as catalysts for fine chemical synthesis has been another major topic: e.g. Cu-HZSM-5 was used by the group of *G. Perot* (Poitiers) for regioselective exchange of halogen atoms in aromatics and *R. Sheldon* (Delft) talked in a convincing way about zeolite-catalyzed rearrangements. *A. Liebens* from the group of *W. Hölderich* (Aachen) presented the selective rearrangement of α -pinene oxide to campholenic aldehyde, an important intermediate in fragrance synthesis. By examination of various zeolites and transition-metal oxides the synthesis of the aldehyde could be optimized up to 80% yield.

Amino-group-functionalized MCM-41 type silicas were presented as solid base catalysts by *M. Lasperas* (Montpellier) for *Knoevenagel* condensations. More basic solid superbases were prepared by *G. Suzuki et al.* (Sumitomo Chemicals) and applied for double-bond isomerizations and side-chain alkylations of toluenes. Ionization of sodium metal on the aluminate-based catalysts is supposed to play a key role for extreme basicity. A disadvantage of this type of catalysts is still the rapid deactivation even with traces of water, oxygen, or carbon dioxide.

Friedel-Crafts acylations are still an important research topic. The use of heterogeneous catalysts, especially zeolites, is obvious advantageous compared to classical stoichiometric amounts of *Lewis* acids. In this context, *L. Delaude* (Swansea) presented new results on the acylation of aryl ethers and tetrasubstituted olefins. While superior yields of the corresponding products were obtained for the first case with H β zeolite, zeolite HY gave the best results for the latter case. Other acylations were described by *M. Spagnol* (Rhone-Poulenc) and *M. Guisnet* (Poitiers). Interestingly, the group of *M. Spagnol* reported in their poster the first industrial realization of zeolite-catalyzed acyla-

tion reactions of aryl ethers. Here, anisole and veratrole were efficiently acylated in liquid phase by acetic anhydride, giving rise only to the *para*-isomer. Alkylations of carbonyl compounds with heterogeneous catalysts were shown from *F. Fache* of the group of *M. Lemaire* (Villeurbanne) and *M. Spagnol* (Rhône-Poulenc). The first group demonstrated the possibility to use reductive *O*- and *N*-alkylations as an alternative catalytic method to stoichiometric nucleophilic substitution, while the latter showed a new process for selective *C*-alkylation of ketones.

Titanium-containing zeolites and aerogels were investigated with hydrogen peroxide as oxidant for sulfoxidation of thioethers by *P. Moreau* and coworkers (Montpellier) and for the oxidation of cycloalkenones by *A. Baiker et al.* (ETH-Zürich): here, amorphous, high-surface titania-silica aerogels provide good selectivities and high activities for epoxidation of bulky electron-deficient olefins. The aerogels prepared by a solgel process and semicontinuous extraction with supercritical CO₂ are better catalysts compared to the corresponding xerogels. A new way to *N*-heterocycles was outlined by *U. Armbruster et al.* (Karlsruhe): the cycloamoxidation of 1,3-pentadiene on V-Mo-P-mixed oxides leads to mixtures containing up to 26% pyridine or 23% 2-cyanopyrrole as the major organic products. Unfortunately, the mechanism of this reaction is still unclear.

Apart from oxidations, catalytic hydrogenations still constitute one of the most important methods for fine chemical synthesis. Besides the already mentioned process for Metolachlor, a couple of other hydrogenations were presented: *K.R. Westerterp* (Twente) talked about the design of catalytic hydrogenation reactors. A comparison of three kinds of continuous reactor types was made for the hydrogenation of nitro-aromatics, especially 2,4-dinitrotoluene. It turned out that the packed bubble column reactor gave the best results for this reaction. Other reductions of nitroarenes were presented from the groups of *P. Rys* (ETH-Zürich) and *G. Neri* (Reggio Calabria). Here, selective hydrogenations of 4-nitroazobenzenes to 4-aminoazobenzenes and of 2,4-dinitrotoluene to nitroarylhydroxylamines, respectively, were of interest.

Claus (Tricat. Ind., Leuna) presented results on the selective hydrogenation of α,β -unsaturated aldehydes. Silica- or alumina-supported silver catalysts favor hydrogenation of the C=O bond compared to the C=C bond. Asymmetric heterogeneous hydrogenation of functionalized C=O and

C=C groups was the subject of several posters. Here, *M. Besson* (CNRS, Villeurbanne) described aromatic hydrogenations of enantiomerically pure *o*-methyl benzoic-acid amides. Selectivities up to 60% were achieved. Both the nature of the support (Al₂O₃ > C) as well as addition of amines influence the diastereoselectivity. Another approach towards selective hydrogenation of aromatics, especially 4-(*tert*-butyl)phenol was described by *J.A. Lercher* (Twente), who used rhodium nanoscale particles stabilized by a polymer (PVP). Catalysts with a low dispersion produced preferentially cyclohexanone, while those with higher dispersion yielded preferentially cyclohexanols. Finally, modelling of asymmetric hydrogenation reactions was the topic of the lecture by *D.G. Blackmond* (MPI, Mülheim). She showed that the application of a simple kinetic model can rationalize effects of hydrogen pressure on enantioselectivities.

In summary, the symposium presented a state-of-the-art collection on heterogeneous catalysis and selected homogeneous fine chemical processes. The organizers managed in an excellent manner to bring together industry and academia. It was shown that 'high level science' and practical application do not exclude one another, but even stimulate each other. Hopefully, the next 'International Symposium on Heterogeneous Catalysis and Fine Chemicals' will continue this way.

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