

CONFERENCE

10th International Symposium on Relations between Homogeneous and Heterogeneous Catalysis (SHHC 10)

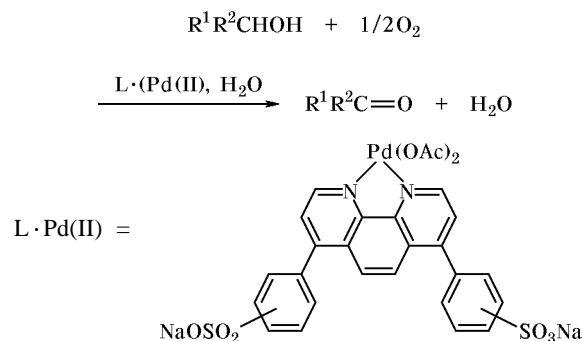
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The 10th International Symposium on Relations between Homogeneous and Heterogeneous Catalysis was held on July 2–6, 2001, in Lyon (France) under the chair of Prof. J.M. Basset. This symposium always attracts attention of chemical companies which have a need for new efficient catalysts. On the other hand, the interdisciplinary character of that field of chemistry makes it interesting for specialists engaged in various branches of chemistry. At present, the problem of “heterogenization” of homogeneous catalysts attracts a specific interest. Innumerable publications on this topic have appeared, which cover both heterogenization of metal-complex catalysts (so-called *surface organometallic chemistry*), and immobilization of Lewis acids and bases. Such heterogenizations are effected by various methods, and their goal is to combine all advantages of homogeneous catalysis (such as efficiency and selectivity) with those of heterogeneous catalysis (such as stability, easy separation from the product, and the possibility for recycling). Insofar as most reports were nevertheless concerned with heterogeneous catalysis and hence with problems of inorganic chemistry (though some organic catalytic reactions were also considered, as a rule oxidation of alcohols, hydrogenation of olefins, hydro- and alkoxy-carbonylation, and polymerization), only those reports which are more closely related to organic chemistry will be discussed.

Four plenary lectures and about fifteen invited lectures were read. Just these lectures were concerned mainly with problems of homogeneous catalysis as applied to organic reactions. T. Marks (USA) reported on cationic metallocene catalysts (single-site catalysts) capable of effecting polymerization of millions of olefin molecules, which were converted into even more powerful multiple-site catalysts with several metallic centers. Such catalysts can be immobilized on a support, and, together with new co-catalysts, they represent a new generation of catalysts capable of simulating organometallic compounds on a surface.

The lecture of R.A. Sheldon (The Netherlands) dealt with catalytic oxidation of secondary alcohols in a biphasic system by the action of sodium hypochlorite in the presence of surface-immobilized piperidine-*N*-oxyl (PIPO) or under catalysis by the system Ru(II)(or CuI)–TEMPO(or PIPO). Below is shown the palladium catalyst proposed for aqueous biphasic oxidation of olefins and alcohols with oxygen. The catalyst may be reused after phase separation.



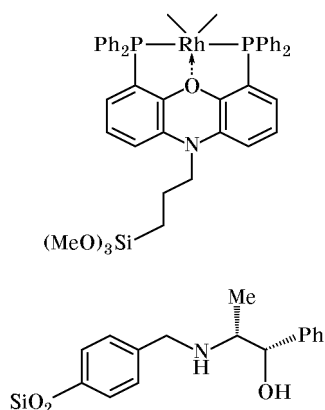
Problems of asymmetric catalysis were considered by E.N. Jacobsen (USA). With the use of numerous examples (opening of epoxy ring, oxidation, addition, etc.), it was demonstrated that the yield and optical purity of products increase in the presence of bimetallic catalysts instead of usual unimetallic ones.

Only the last (forth) plenary lecture read by G. Ertl (Germany) concerned classical heterogeneous catalysis. The lecturer considered the application of scanning tunneling microscopy and other physical methods for studying the surface of single crystals.

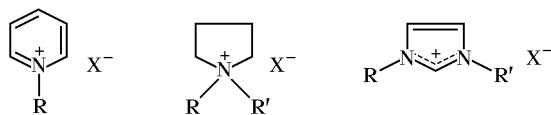
The topic of Marks' lecture was extended by J.C. Stevens (Dow Chemical Co.) who showed the possibility of using the counterion of an immobilized metallocene catalyst, so-called homogeneous catalyst in heterogeneous environment. H. Turner (SYMYX Technologies) demonstrated a wide potential of combinatorial search for homogeneous and

heterogeneous catalysts of olefin polymerization and oxidative dehydrogenation of ethane.

Although methods of immobilization of homogeneous metal-complex catalysts are the subject of extensive studies and numerous examples of such catalysts have already been reported, they are not used so far in large-scale processes. As was noted by P.W.N.M. van Leeuwen *et al.* (The Netherlands), the reason is that two problems are to be solved: metal leaching and moderate catalytic activity. The author considered two examples of silica gel-immobilized selective catalysts which remained highly active over a period of several days. Below are shown the structures of the rhodium complex for hydroformylation and of the immobilized amino alcohol ligand of Noyori ruthenium complex which promotes enantioselective reduction of ketones:



Some problems of homogeneous catalysis may be solved by using ionic liquids as solvent in catalytic processes. This topic was the subject of the lecture of H. Olivier-Bourbigou (France). Structures of some compounds consisting of an organic cation (*N,N'*-dialkylimidazolium, *N*-alkylpyridinium, and *N*-alkyl-tetrahydropyrrolium) and various (usually inorganic) anions are shown below:



X = BF₄, RF₆, SbF₆, CF₃CO₂, CF₃SO₃, Al₂Cl₇, AlCl₄, BR₄, etc.

The author demonstrated the application of ionic liquids in oligomerization of olefins (Difasol process) and hydroformylation.

The use of homogeneous metal-complex catalysis in fine organic synthesis was considered in some lectures: “Molecular Ruthenium Catalysts: From

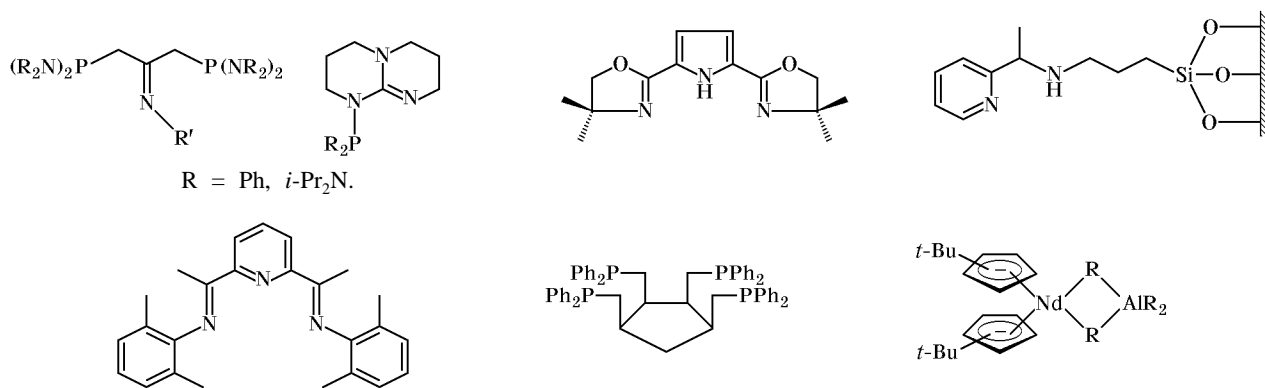
Alkene Metathesis to Selective C–C Bond Formation” (by P.H. Dixneuf, France); “The Catalysis by Transition Metal Complex in Fine Organic Synthesis” (by I.P. Beletskaya and A.V. Cheprakov, Russia); “Advances and Adventures in Oxidation Reaction” (by M. Beller, Germany); and “Manipulation of C–H Bonds for Organic Synthesis. New Ruthenium Complex Catalyzed Reactions” (by S. Murai, Japan).

Reports on various kinds of automatic reactors–analyzers capable of effecting screening of a large number of reactions for a short time aroused a natural envy.

Numerous oral communications and posters dealt with various supporting materials, their modification, and methods of immobilization of transition metal complexes thereon; the application of silica gel and zeolites for this purpose was the most successful. Presumably, just that field will receive especially extensive development in the nearest future. It is important that fairly high values of enantiomeric excess were obtained in some reactions (e.g., epoxidation) under heterogeneous conditions. In this connection, various kinds of enantiopure beads attract interest. For example, a polymer containing optically active amino alcohol moieties was used in the reduction of ketones with isopropyl alcohol in the presence of ruthenium complex.

In some cases, a deep insight was got into the nature of catalytic centers formed by catalyst on a support surface (“Design of Catalytic Sites at Surfaces by Molecular Imprinting and Metal Complexes,” by Y. Iwasawa, Japan). Selectivity is the main problem in catalytic oxidation and acid–base reactions. It is now clear that control of activation and reaction intermediates is critical in achieving selectivity. A way of solving this problem involves the use of organometallic and inorganic complexes as catalyst precursors.

New ligands, including fluorinated chiral ligands, have been proposed. Their complexes with Mn(III) were used in asymmetric epoxidation of alkenes. Some fluorinated ligands were applied to biphasic systems or supercritical carbon dioxide, e.g., in the Rh-catalyzed enantioselective hydroformylation of styrenes. Below are given the structures of interesting ligands having phosphino and imino groups, dihydrooxazole and pyrrole rings, nitrogen-containing ligand immobilized on silica gel surface, sterically hindered diiminopyridine ligand, and *cis,cis,cis*-1,2,3,4-tetrakis-(diphenylphosphinomethyl)cyclopentane (Tedicyp) which ensured all-time high turnover numbers in Pd-catalyzed allylic amination, allylic alkylation, and Suzuki cross-coupling. The first example of



neodymocene-catalyzed copolymerization of ethylene with 1,3-butadiene should also be noted.

Undoubtedly, organization of such conferences is an important task, and participation therein of

chemists from Russia (where heterogeneous catalysis is traditionally highly developed but studies in the field of homogeneous catalysis remain on a considerably lower level) is practically feasible and urgent.