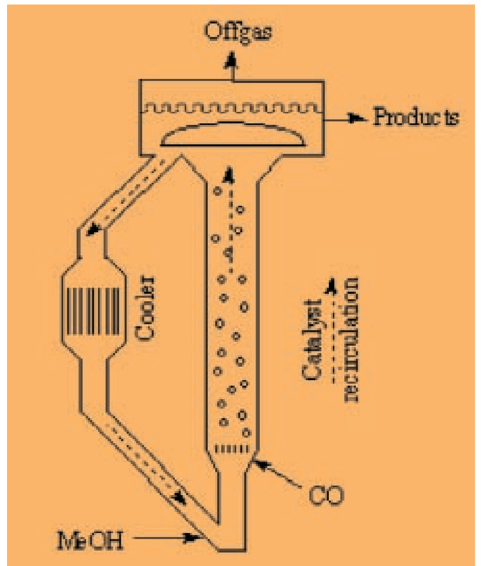


Benedetto Corain, Istituto di Scienze e Tecnologie Molecolari, CNR - Sezione di Padova e Dipartimento di Scienze Chimiche - Università di Padova; Paolo Centomo, Marco Zecca, Dipartimento di Scienze Chimiche - Università di Padova.
benedetto.corain@unipd.it

HYBRID PHASE METAL CATALYSIS BASED ON CROSS-LINKED FUNCTIONAL POLYMERS

Past Expectations and Present Prospects

Hybrid-phase metal catalysis has been a craved goal in chemical processing for more than thirty years.

Materials for hybrid-phase metal catalysis are intended to act as homogeneous catalysts at the microscopic (actually molecular) level and as heterogeneous ones in the macroscopic scale. After more than three decades of both industrial and academic extensive research, the recent outcome of the Acetica Process (Chiyoda and UOP) in the industrial carbonylation of methanol discloses brilliant prospects to hybrid-phase metal catalysis in industrial chemistry.

This short report is the outcome of a critical selection of topics from a huge literature collection gathered since the early Seventies. The selection was based on the personal view of the authors on the title subject and therefore is far from being exhaustive (even in terms of cited *review* papers). In spite of this, it is our opinion that it is representative enough to make possible a reasonable survey of the field. The chemical behaviour of a relatively limited number of metallic elements both in their zero or middle-low positive oxidation state play a pivotal role in modern industrial catalysis (1-6). Three basic groups of metal catalysts may be envisaged:

i) self-supporting (**SS**; tipically heterogeneous);
ii) supported (**S**; tipically heterogeneous);
iii) single site (**SiSi**; tipically homogeneous).

In the frame of this division, we like to point out that

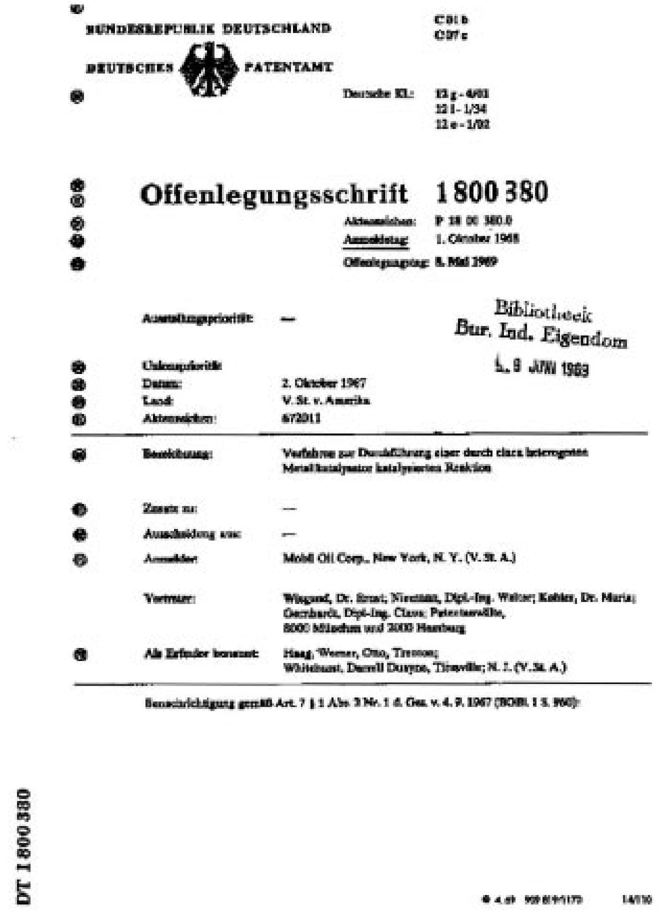
a) typical **SS** catalysts are platinum metal (gauze, oxidation of NH_3 to NO_x), silver metal (particles, oxidation of methanol to formaldehyde), zeolites (particles, Fluid Catalytic Cracking of heavy alkanes), alumina (particles, various applications), acidic ion-exchange resins (MTBE synthesis);
b) typical **S** catalysts are metal nanoclusters (7, 8) supported on inorganic oxides, e.g. platinum(0) on γ–alumina (catalytic reforming of alkanes), iron(0) on oxides (ammonia synthesis), noble metals on monoliths (automobile catalysts for exhaust gases), palladium(0) on active carbon or metal oxides (innumerable applications mainly in hydrogenation reactions), etc.;
c) typical **SiSi** catalysts are metal co-ordination compounds (metal complexes) that as individual, structurally well identified molecular species are known to exert a specific catalytic action, which is often well defined (understood) in a mechanistic sense (5, 6).

When we move from definitions to chemical processing, it becomes quite apparent that **SS** and **S** catalysts are tipically heterogeneous, in that they are particularly well suited for being employed in continous processes. On the contrary, **SiSi** catalysts are tipically homogeneous and not suitable, *per se*, for being employed in continous processing. Continuous operation calls for dedicated specific technological interventions, which often make the use of **SiSi** catalyst uneconomic.

The question of hybrid phase catalysis: preliminary remarks

For both **SS** and **S** catalysts it is expected that the individual activation steps are exerted by the catalyst surface (2, 3) that means by *sets of surface atoms* and not by *single surface atoms*. A very interesting case, which has recently stirred worldwide interest , is provided by the highly chemoselective oxidation of CO to CO_2 by dioxyge catalyzed by nanoclustered Au^0 supported on TiO_2 or Fe_2O_3 (9-11). It is strongly believed that surface Au atoms and oxide "ions*" at the nanocluster-support contact point* do co-operate in the catalyzed reaction. Although the details of this co-operative effect are not yet fully established, the co-operation of Au^0 atoms and oxide surface ions in unquestioned.

On the basis of the above, it is quite clear that a molecularly well defined chemically and mechanically robust catalyst able to behave as a heterogeneous one at the macroscopic level and as a homogeneous one in the nanoscopic scale would be a "holy Grail" in industrial catalysis. Although this idea could not so clearly perceived in the middle of the Sixties, it fostered the imagination of two industrial scientists of Mobil Oil, W.O. Haag and D.D. Whitehurst, (12). They pursued the ambitious goal of preparing innovative catalysts, soon after referred to as "hybrid-phase catalysts" (13), based on the concept outlined above. The cover of one of the three relevant patents filed by Mobil in 1967 and issued in 1969 is reported in Figure 1. The impact of these new ideas with the scientific community was very strong, perhaps inimmaginable today and triggered a sort of worldwide rush to the "perfect" catalysts. Its long wave is still quite evident nowadays in current literature and, fortunately, it also brought out an extremely positive industrial outcome, the *Acetica Process* (14, 15). It is anticipated here that the hybrid catalyst for this process is based on an organic resin as the support. Organic resins were employed also in the very first investigation at Mobil on practicability of hybrid catalysis as a chemical technology. For these reasons and in view of the authors' personal background, only resin-based hybrid catalysts will be covered in this account.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9 JUNI 1969

Unionspriorität
Datum: 2. Oktober 1967
Land: V. St. v. Amerika
Aktenzeichen: 672011

Bezeichnung: Verfahren zur Durchführung einer durch einen heterogenen Metallkatalysator katalysierten Reaktion

Zusatz zu: —
Ausscheidung aus: —
Anmelder: Mobil Oil Corp., New York, N. Y. (V. St. A.)
Vertreter: Wiegand, Dr. Ernst; Niemann, Dipl.-Ing. Walter; Kohler, Dr. Maria; Gernhardt, Dipl.-Ing. Claus; Patentanwälte, 8000 München und 2000 Hamburg
Als Erfinder benannt: Haag, Werner, Otto, Trenton; Whitehurst, Darrell Duayne, Titusville; N. J. (V. St. A.)

Benachrichtigung gemäß Art. 7 § 1 Abs. 2 Nr. 1 d. Ges. v. 4. 9. 1967 (BGBl. I S. 960):

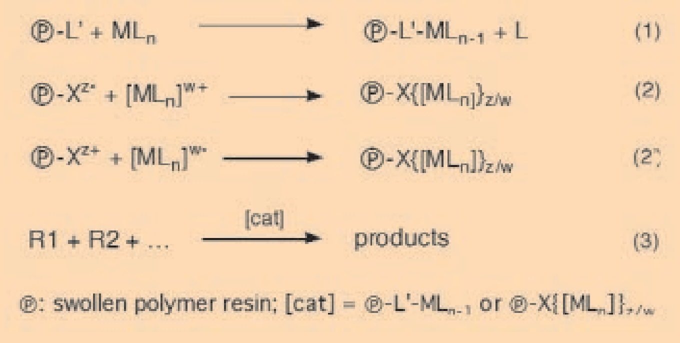
DT 1 800 380

Figure 1 - Cover of one of the 1967 seminal patents to Mobil (Haag and Whitehurst inventors) on hybrid-phase catalysis

The original proposal by Haag and Whitehurst for the preparation of hybrid catalysts was based on ionic interactions between charged metal complexes and fixed ionic sites in organic ion-exchange resins. However, the approach to the heterogenization of **SiSi** catalysts based on electrostatic interaction was soon abandoned, also by Mobil itself. It was believed that ionic bonding would have been too labile and would have lead to catalysts unstable with respect to metal leaching.

At the time the comparative ease of functionalization of organic resins was already well known (cfr. Merrifield resins) and materials like phosphinated polystyrene resins became readily available. Therefore covalent resin-metal bonding, estabilished through metal coordination, became the preferred way to the heterogenization of **SiSi** catalysts. Paradoxically, whereas the covalent bonding approach has not yet brought out any industrial achievement, the first (and to date the only one) industrial hybrid catalyst is based on the approach of ionic bonding. In chemical terms the two approaches are illustrated in Scheme 1.

Ⓟ-L′ or Ⓟ-$X^{z(+;-)}$ stands for a functional insoluble polymer. This is typically a functional resin (16), where L′ is a metal- ligating group (such as a phosphine, a nitrile, a pyridyl, an isocyanide) and X a cationic (such as tetraalkylammonium) or an anionic (such as sulphonate) group. Ion-exchangers became widely commercially available in the late Fifties and early Sixties (17), but were not utilized at the time for catalytic purposes. Resins with metal-ligating functions were developed since the Seventies and some of them also became commercially available (e.g. phosphinated polystyrene/divinylbenzene resins). In spite of the formal simplicity of chemical equations 1-3, the successful immobilization of a **SiSi** catalyst and its subsequent use rest on the delicate balance among many different factors. First of all, the hybrid catalyst must be very stable with respect to metal leaching. Therefore, equilibrium in reactions 1-2′ must lie far to the right. If the metal-resin bond is not strong enough, even low-concentrated impurities in the stream of reactants and products could displace the metal from support. In the case of batchwise operation a strong metal-resin bond is a necessary condition for the recycling of the hybrid catalyst or for its effective separation. This point can be of great importance in fine chemistry applications of hybrid catalysis. Interest in this field and generally in supported catalysis as



$$\text{Ⓟ-L}' + \text{ML}_n \longrightarrow \text{Ⓟ-L}'\text{-ML}_{n-1} + \text{L} \qquad (1)$$

$$\text{Ⓟ-X}^{z-} + [\text{ML}_n]^{w+} \longrightarrow \text{Ⓟ-X}\{[\text{ML}_n]\}_{z/w} \qquad (2)$$

$$\text{Ⓟ-X}^{z+} + [\text{ML}_n]^{w-} \longrightarrow \text{Ⓟ-X}\{[\text{ML}_n]\}_{z/w} \qquad (2')$$

$$\text{R1} + \text{R2} + \ldots \xrightarrow{[\text{cat}]} \text{products} \qquad (3)$$

Ⓟ: swollen polymer resin; [cat] = $\text{Ⓟ-L}'\text{-ML}_{n-1}$ or $\text{Ⓟ-X}\{[\text{ML}_n]\}_{z/w}$

Scheme 1 - Schematic illustration of the rationale of hybrid phase catalysis

applied to fine chemistry is steadily growing (18). This is by no means surprising, because environmental issues urge stoichiometric synthetic methods to be replaced by catalytic ones. **SiSi** catalysts represent a viable solution to this problem, but quite often they are very sophisticated and expensive materials. This calls for efficient recovery and in this connection their heterogeneization can be highly desirable. The catalyst as a whole, $\text{Ⓟ-L}'\text{-ML}_{n-1}$ or $\text{Ⓟ-X}\{\text{ML}_n\}_{z/w}$, must be molecularly accessible to reagents in the swollen polymer framework. In particular the metal center must be reached by reagents and left by products with no or acceptable mass transfer limitation. For this reason, the employed resins, which are insoluble, must exhibit some degree of swelling in the reaction medium. Swelling of crosslinked polymers occurs in suitable solvents and therefore hybrid resin based catalysts are are to be used under liquid-solid or gas-liquid-solid conditions. If ML_n is a **SiSi** active catalyst, preservation of its activity and selectivity implies that immobilization does not alter its molecular structure. Therefore, features like oxidation state and coordination number of the metal, type of ligands in the coordination sphere, nuclearity of the immobilized metal species, and so on, in the hybrid catalyst should be ideally the same as in the parent **SiSi** catalyst. The simultaneous fulfillment of all these requirements is very difficult to achieve. Under this respect ionic bonding is apparently better than covalent bonding. The ion-exchange process (equations 2 and 2') does not necessarily imply changes in the coordination sphere of the metal. Moreover the stoichiometry of the anchoring reaction is simply dictated by the charge ratio. In the case of immobilization of a **SiSi** catalyst by covalent metal bonding (equation 1), the control of the number of L' entering groups and of displaced L ligands is not as easy. This can lead to substantial rearrangements of the metal species. Last, but not least, hybrid catalysts must be mechanically and thermally resistant, in particular if designed for continuous operation. Under this respect, organic polymers are usually inferior to inorganic solids. However, organic polymers proved to be efficient industrial catalytic materials in a number of cases. In addition to the Acetica process discussed later, at least four other industrial catalytic processes are run with polymeric materials as the support or catalyst. These are the synthesis of MTBE (17) and of bisphenol-A (17) (condensation reactions) catalyzed by acidic ion exchange resins; the deep deoxygenation of water with dihydrogen catalyzed by palladium over ion-exchange resins (17); the synthesis of MIBK from acetone and hydrogen (consecutive condensation and hydrogenation reactions), promoted by a remarkable bifunctional palladium catalyst on an acidic ion-exchange resin (17). Although these processes are not based on hybrid catalysis, they highlight the relevance of organic resins in industrial catalytic chemistry. Inspection of the relevant literature over the last thirty years convinces the authors that the whole of these important facets of hybrid phase catalysis have been to various extent essentially absent from the papers (if not from the minds) of the legions of authors, who generously gathered an enormous amount of experimental data on the subject. In particular, the crucial problem of catalyst stability and re-usability appears to have been faced rather superficially by most authors and this might be the key reason why it took thirty years before the rush to the "perfect" catalyst turned out to reach the first important industrial application.

The historical development of the rush to the "perfect" catalyst as seen from dedicated review papers

In the time-range 1970-1980 the rate of production of research papers and patents was so high that critical and comprehensive reviewing was probably difficult. The first comprehensive reviews appeared in 1977 by Grubbs (13), in 1981 by Sheats (19) and by C.U. Pittmann Jr. (20). They were followed in 1985 by the remarkable book by Hartley (ca. 1,600 references!) (21). In this book a considerable attention is also paid to hybrid-phase catalysts that are based on the anchoring of catalytically active metal complexes to *inorganic* supports. To our knowledge, the last two important reviews of this decade are the 1986 paper by Pittman and Rausch (22) and the 1988 one by Garrou and Gates (23). The decade 1990-2000 was somewhat less productive as compared to the previous one, owing to some decrease of interest of Academy and Industry in the subject. In any case significant reviews are to be cited. The 1996 review paper by Schlick, Bortel and Direk (24) and the 1998 one by Sherrington (25), and in 1999 by Cameron (26). A very important reference chapter by Panster and Wieland was also published in the landmark book co-edited in 1997 by B. Cornils and W. Herrmann, "Applied Homogeneous Catalysis with Organometallic Compounds" (27).

A sudden resurge of interest is featuring the start of this decade as witnessed by the appearance of two major review papers in 2002 by Leadbeater and Marco (28) and by McNamara, Dixon and Bradley (29). A look at the references list of these two papers, 197 and 121 respectivly, reveals that ca. 30% and ca. 25% respectively of them refer to papers that appeared in years 2000-2002! The interested reader will find the benefit to discover in their extensive references list other significant review papers not mentioned in this section.

The unawareness of the issues of nanomorphology, molecular accessibility, mechanical stability and chemical stability of $\text{Ⓟ-L}'\text{-ML}_n$ catalysts

It was mentioned above that resin-based hybrid catalysts need a swelling liquid agent to work efficiently and therefore they are invariably employed under liquid-solid or gas-liquid-solid conditions. To the best of our knowledge, research carried out sofar in the field did almost completely neglect the question of the *morphology of the macromolecular support at the nanometer scale* in the swollen (working) state of the catalyst. The experimental work was generally aimed at anchoring the desired ML_n molecular catalyst to a chosen support, very finely characterizing the obtained macromolecular catalyst $\text{Ⓟ-L}'\text{-ML}_n$ from a physico-chemical point of view (24) but looking at it as a *molecular* rather than a *macromolecular entity* (*vide infra*) and trying immediately its catalytic productivity to be evaluated in terms of activity and selectivity. Re-usability is often reported in very qualitative terms, if any, and mechanical stability, as a specific piece of information, is normally a mistery. In spite of these circumstances, synthetic results are sometimes good and promising, but the very issue of catalyst chemical stability and prospects to technological developments normally do not appear among the conclusions of the paper. As a contribution to a more complete way of looking and evaluating the potentialities of hybrid phase catalysts based on functional resins, we will shortly summarize in these section their major macromolecular features (17). Functional resins (FR's) are isotropic materials, often commercialized as submillimetric beads, brittle in nature, built up with macromolecular chains, chemically interconnected by covalent bonds or particularly effective hydrogen bonds or physically thoroughly entangled. Synthetic resins are typically functional ones, i. e. built up with polymer chains bearing molecular pendants that can be designed to perform a chemical task. Depending on their micro- and nanoscale morphologies FR's are classified as either microporous (gel-type) or macroporous (macroreticular) (30).

Gel-type resins do not possess any porosity in the dry state (glass-like). Upon swelling they develop an extensive nanoporosity (Figure 2). This is relevant to the catalytic activity of any hybrid catalyst based thereof, because the swollen state that is the working state of these materials. Macroreticular resins do possess a microporosity (i.e. a porosity at the micrometer scale) in the dry state. Upon swelling they develop also a certain degree of nanoporosity, but in this case the phenomena are limited to thin surface layers of the permanent micropores. These swollen regions are the actual working "arena" of the catalysts. The control of the chemical structure of the resins is a major tool for tuning their swelling ability in proper fluid media, a pivotal aspect of their utilization (39). Upon switching from polar to unpolar pendants, specific swelling volume changes dramatically (31). Therefore pendants, in addition to their function of "molecular hooks" (Scheme 1), play also a critical physico-chemical role both in the anchoring of the desired ML_n species and in the catalytic reactions. Not only their nature affects the swelling behaviour, i.e. the accessibility of the polymeric network, but even the *thermodynamics* and the *intrinsic kinetics* of a given catalytic reaction occurring in the swollen resin domains (32). It could be difficult to match all these conditions with FR's containing only one kind of functional groups acting as pendants. However, in polymer chemistry it is relatively easy to have more than one kind of pendant in the same materials (e.g. in copolymers) and this allows to tailor the polymeric support to the desired application.

Also porosity and thermal stability should be recognized as fundamental properties and properly considered in catalyst design. The overall nanoporosity of gel-type resins (Figure 2) can be reasonably modulated upon controlling resins cross-linking degree (17, 33, 34) and, consequently, the accessibility of the interior of their particles may be finely controlled (see below). The same holds for macroreticular resins the porosity of which can be controlled with appropriate synthetic procedures (30). Thermal stability can be a critical point in the case of organic resins. However, it is not uncommon to observe appreciable thermal stability under nitrogen up to 300-400 °C (35), as widely confirmed in these laboratories for polyacrylic resins. The general question of the molecular accessibility of the active sites (i.e. the immobilized metal complexes) in hybrid catalysts lies behind the above discussion. In recent years (17, 33, 34) we have addressed this issue from a general point of view. To this purpose we developed a

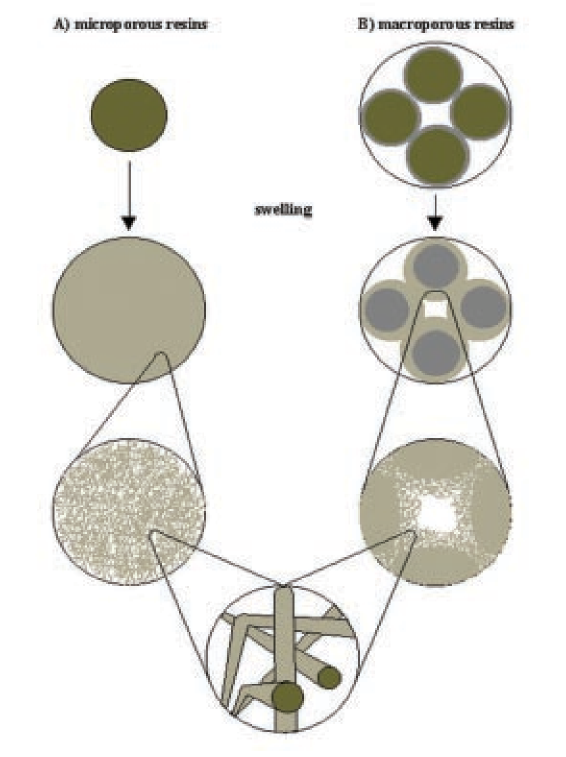


Figure 2 - Schematic representation of the micro- and nanoscopic morphology of gel-type (microporous) and macroreticular (macroporous) resins

multi-methodological approach for connecting the nanostructure of gel-type and macroporous resins in their swollen state to their molecular accessibility (36). Our approach is based on the combination of ISEC ("Inverse Steric Exclusion Chromatography") (37, 38), ESR (spin probing (39) with TEMPONE, 2,2,6,6-tetramethyl-4-oxo-1-oxyl-piperidine) and PGSE NMR ("Pulse Field Gradient Spin Echo Nuclear Magnetic Resonance") (34, 36) techniques (Figure 3). ISEC detects the nanoscale morphology of swollen polymers, in terms of spatial distribution of polymer chain segments. ESR and PGSE NMR measurements allow the assessment of rotational and translational mobility of molecular probes, which are expected to depend on the available free space among polymeric chains. In swollen resins this space is not void, but actually "filled" by the swelling agent through which molecular probes can diffuse. In the investigated FR's we were able to obtain quantitative correlations between the morphology and the molecular mobility at the nanometer level.

Our results are in agreement with observations from other laboratories (17) and strongly support the description of swollen frameworks as more or less viscous "solutions" of (interconnected) polymer chains that *define a size-controlled polymer framework*. The functional pendants or supported metal complexes located within this network *can be* molecularly accessible to given reagents or catalytic centers and consequently able to perform chemical work. In 1988, compelled by the apparent carelessness in the literature about these issues, A. Guyot wrote that "It is then no longer possible to depict the polymer support as a simple letter **P** surrounded by a circle, as has often been done before. It is also no longer possible to consider the support as a rigid and inert material like a stone cast into the liquid medium" (39). Although we did the same also in this report, for sake of simplicity, we completely adhere to Guyot's statement. We are aware that the properties of would-be polymeric supports must be taken into account in designing resin-based catalysts. Therefore, we had been committed to find proper methods for the assessment thereof (see above). Unfortunately, we must also record that fifteen years later Guyot's statements things do not seem to have changed much. The "trial and error" approach seems to be still the dominating way of thinking. Even the admirable references 28 and 29, surprisingly indeed, do exhibit the total absence of any concern of this kind.

A second basically neglected critical issue in the past and present literature is the issue of mechanical stability of these catalysts. The mechanical robustness of the catalyst plays a decisive role in case of real chemical processing and convenient solutions must be discovered to expand the scope of hybrid catalysis as an industrially relevant chemical technology. This issue is currently under investigation in our laboratories (40).

The importance of the chemical stability of hybrid catalysts towards metal leaching has been already underlined in the Introduction. From the point of view of thermodynamics, equations 1, 2 and 2' are featured by an equilibrium constant K (hereafter only equation 1 will be taken into account in the discussion). Under the hypothesis that one molecule of **SiSi** catalyst, (ML_n), is taken up per each functional pendant, L', the reaction can be treated just like a Langmuir adsorption process. Therefore the molar fraction of metal co-ordinated sites throughout the particle volume (χ_M, the equivalent of θ in the Langmuir isotherm) and the concentration of free ML_n in solution (the equivalent of partial pressure in the Langmuir isotherm) are simple functions of the formation constant K:

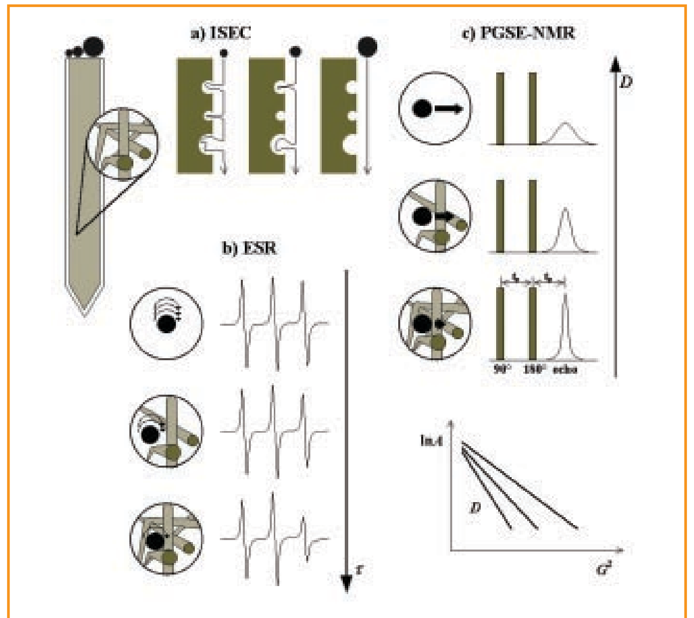


Figure 3 - Expected conceptual interrelation among Isec, Esr, Pgse Nmr information in swollen based metal catalyst

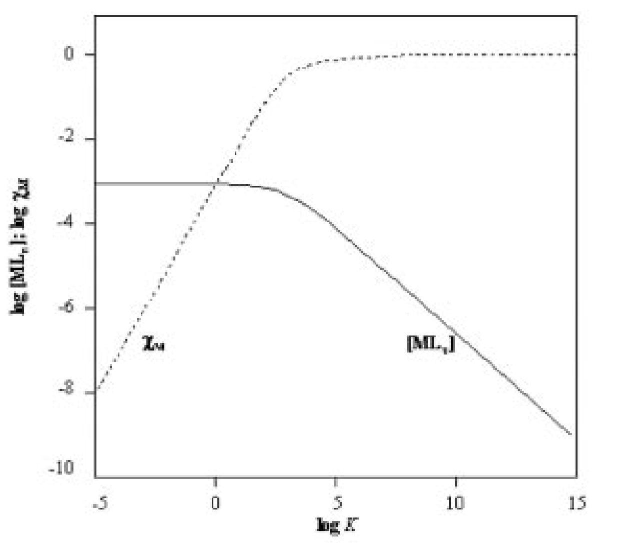


Figure 4 - Plots showing the dependance of log χ_M and of log (ML_n) on the formation constant of the hybrid-phase catalyst, under given conditions (courtesy of Prof. G.G. Bombi)

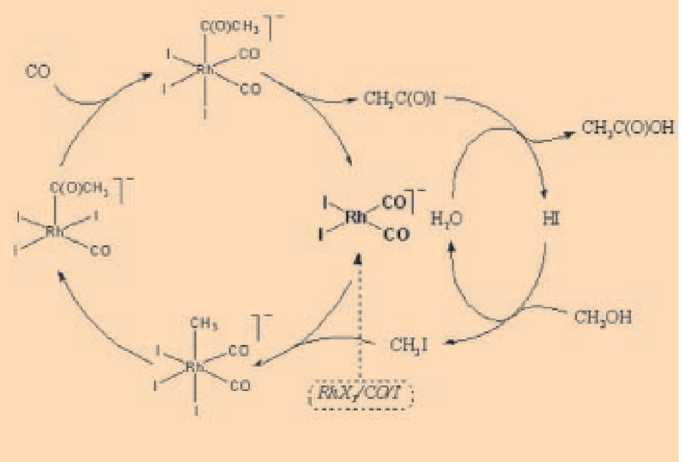
From the plots of log χ_M vs. log K and log (ML_n) vs. log K (Figure 4), it is evident that for relatively dissociation-stable materials, the concentration of free ML_n reaches figures which seem very low (less than 10^{-8} M with $K>10^{15}$). From the analytical point of view, these levels can be considered low indeed, but from the point of view of catalytic phenomena they could not be negligible.

Concentration of a soluble catalyst in the order of 10^{-7}-10^{-8} M might be enough for effective homogeneous catalysis. This can be of the utmost importance for the defense of proprietary rights. In fact, if ML_n is a patented homogeneous catalyst for a given reaction, a new hybrid catalyst obtained by means of its immobilization on a solid support can be patented only if it is demostrated that its activity does not stem from leached ML_n.

In other words it must be proved that the hybrid catalyst is really such and not simply a "trojan horse" carrying a homogeneous one. The analytical detection of metal species in low or trace amounts in complex reaction mixture can be an exceedingly difficult task. Therefore a negative analytical search for them is not conclusive. Fortunately, a fine innovative experimental verification of authentic heterogeneous character of hybrid catalysts was proposed by Sheldon et al in 1998 (41), i.e. the evaluation of the catalytic activity of the liquid phase in equilibrium with the solid catalyst, after filtration of the same at the catalyst under *strictly* operational conditions. We strongly believe that Sheldon's criterion will become a *due test* in future verifications of authentic hybrid-phase catalysts.

From the past technological failures to the potential extensive success of hybrid phase catalysis: the Acetica Process

Around the middle of the seventies Mobil developed, up to the pilot plant stage, a hybrid hydroformylation catalyst based on a rhodium complex supported on an organic resin. Haag and Whitehurst, the aforementioned pioneers of hybrid catalysis, were involved into this project. According to them (42), this catalyst was ready for commercial-scale exploitation when Mobil decided to stop the project only because the market conditions and prospects were not favourable for the expansion of hydroformylation production capacity.



Scheme 2 - The catalytic chemistry of the Monsanto process

In spite of this early demonstration of the technical feasibility of hybrid phase catalysis, this concept did not meet any commercial success until the end of the nineties, when the Acetica process for the production of acetic acid by methanol carbonylation was announced. This is the first process based on a hybrid catalyst ever run into operation and to date the only one.

Acetic acid is a strategic commodity presently synthesized at the level of ca. 8 million t/year scale world wide along four industrial routes (43), the most important of which is the Monsanto process (1970). After improvements by BP-Amoco, Celanese and others, it accounts for more than 60% of the world production. The Monsanto process is a very brilliant example of applied metal co-ordination chemistry and is featured by a remarkable 99% chemoselectivity referred to the consumption of methanol (85% if referred to CO). The underlying chemistry is illustrated in Scheme 2. It is important to appreciate that all the rhodium intermediates intervening in the catalytic cycle are *anionic* species. Despite its remarkable merits, the classical Monsanto process is still affected by a few drawbacks. The most serious one is the relatively large water amount (ca. 15%)

RIASSUNTO

Catalisi metallica di tipo ibrido basata su polimeri funzionali reticolati: passate aspettative e prospettive attuali

L'idea di realizzare catalizzatori metallici atti ad agire a livello microscopico (nanometrico) in fase omogenea e a livello macroscopico in fase eterogenea, catalizzatori "ibridi", ha giustificato numerosissimi progetti di ricerca dal 1967 ad oggi. In termini generali, i tentativi compiuti hanno teso allo scopo di legare complessi metallici noti quali efficaci catalizzatori in fase omogenea (ML_n) *a particelle materiali insolubili in un dato mezzo solvente, molto spesso costituite da resine funzionali* (℗-ML_n)*. A fronte di moltissimi risultati interessanti sul piano accademico, i catalizzatori ibridi hanno solo di recente (1998) raggiunto livelli di interesse tecnologico nella carbonilazione industriale del metanolo ad acido acetico (Processo Acetica, Chiyoda Corporation). In questa rassegna sono esaminati problemi di tipo strutturale e di stabilità chimica, dei catalizzatori* ℗-ML_n *e sono presentate valutazioni pertinenti alle prospettive di sviluppo tecnologico della catalisi ibrida, specialmente alla luce della stabilità del catalizzatore "on stream".*

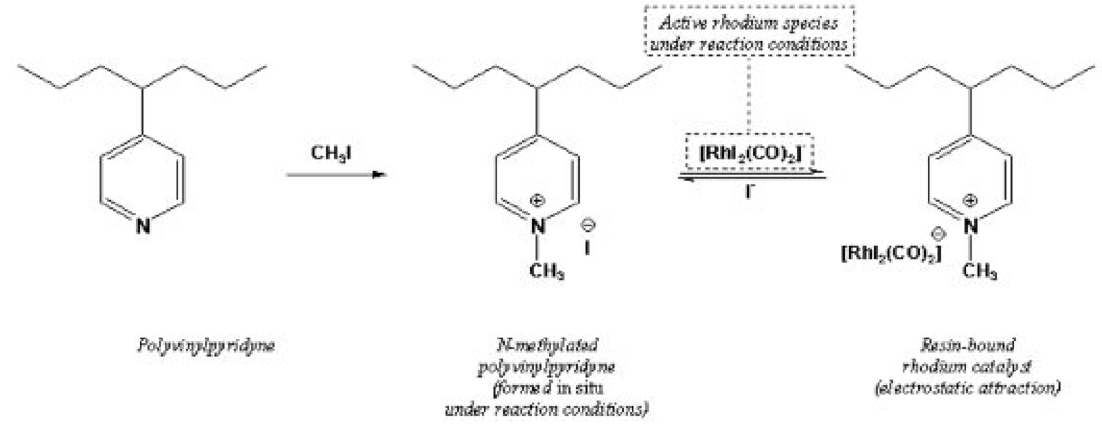


Figure 5 - Sketch of the hybrid-phase catalyst of Acetica Process

required to increase the catalyst's concentration, to which the (homogeneous) reaction rate is proportional.

These conditions favour the WGS reaction, which lowers the chemoselectivity based on CO. Even worse, the removal of excess water for product purification represents a major cost. Moreover, some precious metal goes lost during the catalyst's separation step (flashing). The addition of substantial amounts of metal iodides (e.g LiI) as promoters, introduced by Celanese in the eighties, allows running the reaction with lower water content (down to 2%). Under the conditions of the Celanese process a third iodo ligand adds to $(RhI_2(CO)_2)^-$. The dianionic pentacoordinate intermediate undergoes much more readily oxidative addition of methyl iodide. On the other hand, high iodide concentration brings out corrosion problems in acid aqueous environment and can cause catalyst poisoning in some downstream applications.

The Acetica process, commercialized jointly by Chiyoda and UOP, tackles all these drawbacks in a completely different way. The catalyst is obtained by immobilization of the classical Monsanto soluble rhodium catalyst onto the Reillex 425 polyvinylpyridine resin, a commercially available macroreticular, crosslinked polymer. The hybrid catalyst has comparable activity in comparison with $(RhI_2(CO)_2)^-$. The use of the heterogenized catalyst sweeps away the problems connected to the catalyst's solubility, which is no longer a limiting factor. Therefore, the water content in the Acetica process is lowered down to 3-7%. One of the keys to the success of the Acetica hybrid catalyst is its outstanding stability (more than 7,000 hours on stream at 160-200 °C and 30-60 atm). In fact, other resin-based hybrid catalysts had also shown similar activity, but they were plagued by rhodium leaching and limited resin thermal stability.

Polyvinylpyridine resins are known for their relatively high thermal stability and, quite importantly, they undergo N-methylation by methyl iodide. In this way cationic sites are formed within the polymeric framework and they effectively retain it the metal species involved in the catalytic cycles, just because they are *all negatively charged species* (Figure 5). However not any resin functionalized with pyridinium ions is a suitable one. Drago *et al.*, proposed the electrostatic heterogenization of the Monsanto catalyst with N-methylated co-polystyrene-vinylpyridine as early as in 1981 (44). They observed extensive rhodium leaching, which could be limited (but not suppressed) by substituting benzene for acetic acid/water in the reaction mixture.

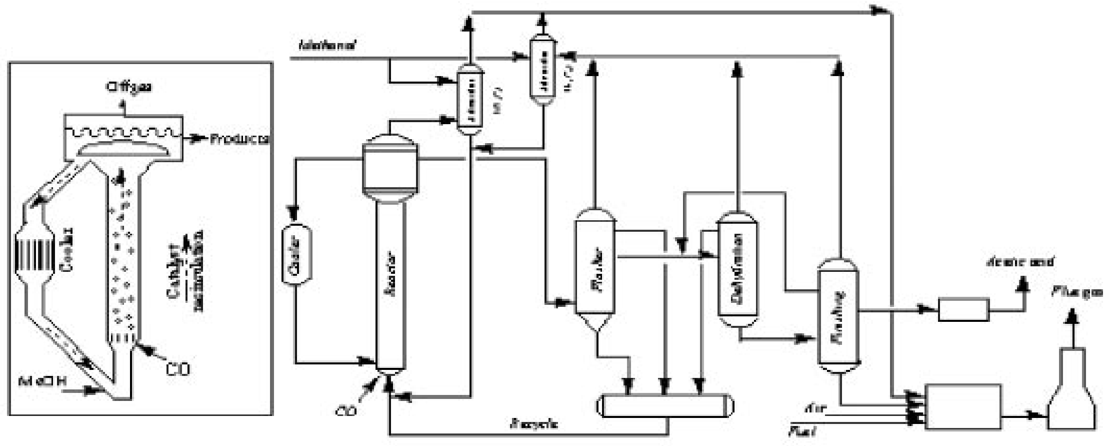


Figure 6 - Reactor system and process diagram of Acetica Process (from (42), with permission)

This underpins the role of the supporting resins, which are not simply solid platforms for the catalyst, but can affect its performance in a number of ways, as outlined before. As chemically smart as it can be, the resin-supported Acetica catalyst would have been useless without proper reactor design.

A general objection to the use of organic polymers as supports for heterogeneous catalysis rests on their low mechanical resistance in comparison with inorganic solids. In the Acetica Process the reaction occurs under three-phase (gas-liquid-solid) conditions and the use of a continuosly stirred reactor could be troublesome for both the catalyst and the reactor. Therefore, a bubble column is applied to keep mechanical stress as low as possible.

The reactants and the catalyst are fed at the bottom of the reactor. The rising fluids drag the catalyst to the top, where it is separated by decantation and recycled through a side heat exchanger (Figure 6).

Conclusions

A single technological success after ca. 30 years of dedicated basic research (how many thousands of papers and patents?) might be considered a modest result. However we believe that times are mature for further prominent steps, most likely in the field of Fine Chemistry. The Acetica process could be the seed of a long series of "good shots". However, the development of industrially successful hybrid-phase catalyst will require a great deal of attention to be paid to catalyst stability and to the very nanostructural and physico-chemical features of the polymer framework. We are also convinced that the wise Sheldon's criterion must be the leit-motive for any future technologically relevant proposal.

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