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From supported homogeneous catalysts to heterogeneous molecular catalysts

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Abstract

Numerous methods are now available for the synthesis of a large variety of heterogeneous molecular catalysts. Their specific domain of application, and the main advantages and drawbacks of these solids are briefly analyzed here.

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1. Introduction

The heterogeneization of homogeneous catalysts is a field of continuing interest: indeed, although some of these organometallic complexes exhibit remarkable catalytic properties (activities and selectivities), they are difficult to separate, intact, from the reaction medium. This problem becomes even more crucial with the recently developed asymmetric catalysts, which rely on very expensive chiral ligands. Thus, unless the activity of the homogeneous catalysts is exceptionally high, their heterogeneization is still currently an economical, but also a toxicological and environmental challenge. To reach this goal, many different strategies can and have been considered, which belong to two major classes:

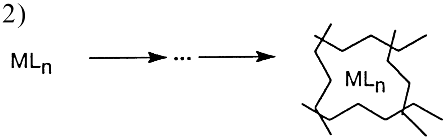
(1) Those which preserve as much as possible the coordination sphere of the metal. This is achieved:

- By anchoring the homogeneous catalyst to an inorganic oxide or an organic polymer via bonds between the solid and one (or more) ligand(s) at a position remote from the atom coordinated to the metal center. (eq. 1)

$$ML_n \rightarrow \rightarrow |\!\approx L'ML_{n-1} \qquad L'\approx L \tag{1}$$

Ligand L′ is a ligand L functionalized so as to allow for a reaction with the support of interest.

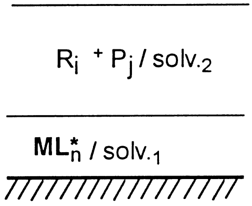
- By encapsulating or encaging the catalyst in the voids of a porous, inorganic or organic, solid: (eq. 2)



(2)

- Or by immobilizing the homogeneous catalyst in a film of solvent (non volatile or hydrophilic) deposited on a solid, while reactants and products are either in the gas phase or in a second solvent non-miscible to the first one. These are the so-called "supported liquid (aqueous) phase catalysts" (SLPC/SAPC) (Scheme 1).

Formally, all these methods lead to the so-called "supported homogeneous cata-



Scheme 1. Principle of SLPC catalysts.

lysts": this means that the structure of the supported organometallic complex is nearly identical to that of the precursor homogeneous catalyst.

(2) Those which anchor the organometallic complex via a direct bond between the metal center and a surface atom: (eq. 3)

$$\mathrm{ML_n} \rightarrow\ \rightarrow\ |\!\approx\!\mathrm{ML_{n\text{-}i}} \tag{3}$$

This procedure induces important changes of the ligand environment around the metal center, which includes now a "solid" ligand. Two situations ought to be considered separately:

- The precursor organometallic complex is an homogeneous catalyst. Then, the supported complex, whose structure can be very different from not only the precursor complex, but also from any known homogeneous catalyst, is as such a new heterogeneous organometallic catalyst.
- The precursor organometallic complex is not a catalyst. It is chosen so that its reaction with the support leads to a clean and precise anchoring of the metal. In a second step, this supported organometallic complex is chemically transformed into a supported molecular catalyst, designed for a given target reaction.

These types of catalysts will be referred to as "heterogeneous molecular catalysts".

We will briefly review these different methods of synthesis of heterogeneous molecular catalysts and show, through a restricted number of examples taken either from the literature or from our own research, the advantages and inconveniences of each one. We will focus on those using inorganic oxides as supports; excellent reviews concerning heterogeneized catalysts on polymer supports have appeared recently, which we strongly recommend to the reader [1–7].

2. Supported homogeneous catalysts

2.1. Catalysts anchored on functionalized solids

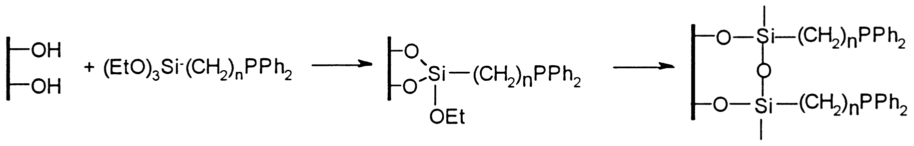
This is certainly the oldest method described in the literature, although the first example did not concern an organometallic complex [$\mathrm{Pt(NH_3)_4^{2+}}$] and used an ionic bond to anchor the complex to the surface (sulfonated silica) [8]. Most of the studies use silica as the support: it presents the advantages to be chemically inert towards many reactants because it has no pronounced surface acidity which would induce secondary reactions, to have surface hydroxyl groups which allow for ligand bonding, to present high specific surface areas and good thermal and mechanical stabilities.

Schematically, two different approaches were used, which are represented below: (eq. 4–5)

$$\vdash\!\mathrm{OH} + \mathrm{X}\!\approx\!\mathrm{L'} \rightarrow \vdash\!\mathrm{O}\!\approx\!\mathrm{L'} \rightarrow \vdash\!\mathrm{O}\!\approx\!\mathrm{L'\,ML_{n\text{-}1}} \tag{4}$$

$$\vdash\!\mathrm{OH} + (\mathrm{X}\!\approx\!\mathrm{L'})\mathrm{ML_{n\text{-}1}} \rightarrow \vdash\!\mathrm{O}\!\approx\!\mathrm{L'ML_{n\text{-}1}} \tag{5}$$

The first method consists in functionalizing the surface of silica by reaction between a bifunctional ligand, $\mathrm{X}\!\approx\!\mathrm{L'}$, and the surface silanols. The X group is chosen



Scheme 2. Possible cross linking surface reactions.

so as to react easily with hydroxyls; it is generally Cl, $SiCl_3$, $Si(OEt)_3$, OH or $SiR'_2(OR)$ [1]. In most cases, L′ is a phosphine, PR'_2R, the R alkyl or aryl substituent bearing the X group.

$$X\sim L' = X\text{-}(CH_2)_nPPh_2 \text{ or } X\text{-}C_6H_4\text{-}PPh_2$$

With X = OH or $SiR'_2(OR)$, a better control of the surface reaction is claimed: the cross-linking reactions are suppressed (Scheme 2) and the stoichiometry of the anchoring reaction is simple [9].

The alkyl chain $(CH_2)_n$ acts as a spacer between the support and the complex: its length allows for a certain mobility of the complex and a partial release of the steric hindrance induced by the support, but it may also be a source, for the larger n values, of catalyst deactivation by dimerization of the active species. It has, thus, a major influence on the activity and the selectivity of the catalyst.

The complex ML_n of interest is grafted on the functionalized solid by a ligand exchange reaction with the surface ligands L′. The donor ligand L in the precursor complex is often a phosphine, or any ligand easy to remove from the system, such as CO [1].

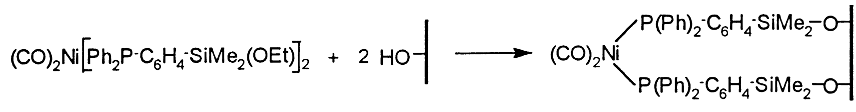
The second approach, described in eq. (5), consists of synthesizing first the complex $ML_xL'_y$, with the desired ratio [functionalized ligand L′]/[M]. This method is only of interest in the cases when the previous one (eq. 4) does not lead to the desired anchored complex, because the syntheses and isolation of these functionalized complexes are not straightforward (oily products are often obtained). One of the successful examples concerns the synthesis of nickel carbonyl complexes anchored to the surface via two bonds in an attempt to increase their stability through a sort of "chelate effect". The simplest method, which consists in reacting $Ni(CO)_4$ with the related phosphinated silica, leads invariably and only to the monophosphine complex, under all tested conditions: (eq. 5)

$$Ni(CO)_4 + PPh_2-C_6H_4-SiMe_2-O-Si\equiv \rightarrow (CO)_3NiPPh_2-C_6H_4-SiMe_2-O-Si\equiv \quad (6)$$

On the other hand, under classical conditions, the complex $(CO)_2Ni[PPh_2(C_6H_4)SiMe_2(OEt)]_2$ reacts with silica mainly via one functionalized ligand as demonstrated by ^{29}Si and ^{31}P CP MAS NMR spectroscopy [10]: (eq. 7)

(7)

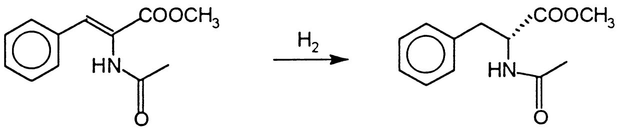
But, when the solution of the complex is added drop by drop to silica, then the desired di-anchored complex is formed [9]: (eq. 8)



$$(CO)_2Ni[Ph_2P\text{-}C_6H_4\text{-}SiMe_2(OEt)]_2 + 2\,HO\text{-} \longrightarrow (CO)_2Ni\begin{array}{l} P(Ph)_2\text{-}C_6H_4\text{-}SiMe_2\text{-}O\text{-} \\ P(Ph)_2\text{-}C_6H_4\text{-}SiMe_2\text{-}O\text{-} \end{array} \quad (8)$$

The success of the method seems, thus, to be very dependent on the precise experimental conditions (surface state of silica, reactivity of the functional ligands, ligand concentration etc.).

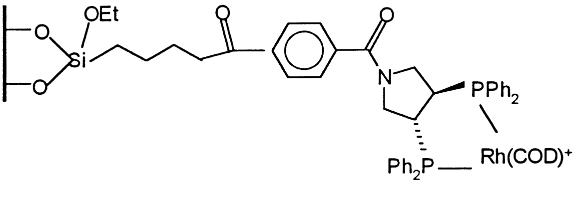
Both methods were successfully used to immobilize enantioselective hydrogenation catalysts. These catalysts are essentially diphosphine Rh(I) complexes; they can achieve enantiomeric purities (ee) as high as 100%. Their heterogeneization implies a modification of the phosphine ligands by introduction a functional group, such as NH or OH which will allow their anchoring on a solid surface. The disphosphine pyrrolidine-based ligands, developed by Nagel [11] and Pugin [12] fulfil this requirement. One of the best so far reported immobilized catalysts (Scheme 3) is synthesized following the second approach (eq. 5): 100% ee is reported for the hydrogenation of methyl acetamidecinnamate [11]. (eq. 9)



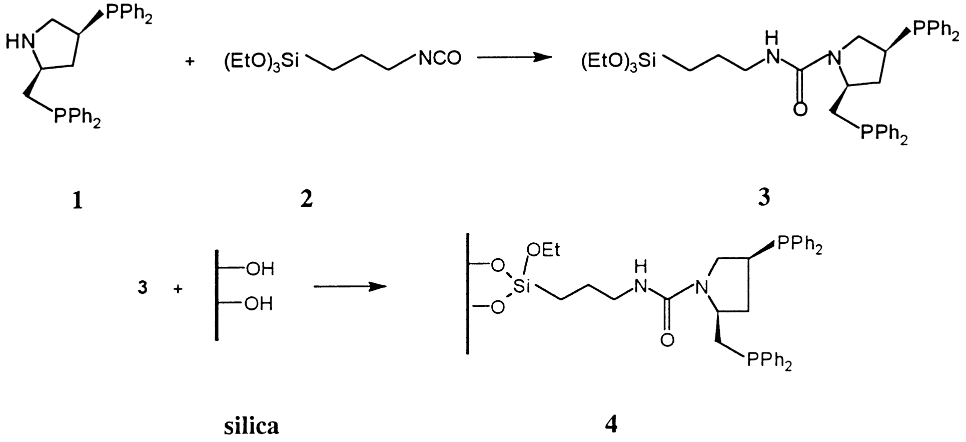
(9)

Similar catalysts, prepared by reaction of the same Rh complex, $Rh(COD)_2BF_4$ with silicas previously functionalized, as described in Scheme 4, give ee's up to 94.5% for the same reaction.

These latter catalysts are, according to their authors, more advantageous because the functionalization is performed from the easily available linker, 3-isocyanatopropyltriethoxysilane, $OCN(CH_2)_3Si(OEt)_3$, and the catalysts are of low "molecular weight". These catalysts are reportedly easy to separate and re-use [12]. Interestingly, the catalysts obtained with these same functionalized silicas from the neutral complexes $[M(COD)Cl]_2$ (M = Rh, Ir) are as active as their homogeneous counterparts, but they show an activity drop with increasing metal loading. This latter effect is correlated to the formation of chloride bridged Rh- or hydrogen bridged Ir- dimers, for the higher metal loadings. As the authors point out, this phenomenon hampers



Scheme 3. Silica anchored enantioselective hydrogenation catalyst [11].



Scheme 4. Method of synthesis of a silica anchored asymmetric ligand according to Ref. [12].

any future industrial application of these latter catalysts because their productivity (expressed as volume substrate converted/volume catalysts) is too low and leads to severe handling problems [12].

In conclusion, this general type of supported homogeneous catalysts, i.e. the catalysts anchored to a solid via a ligand, was tested for a number of reactions, including hydrogenation, hydroformylation, hydrosilylation, isomerization, dimerization, oligomerization and polymerization of olefins, carbonylation of methanol, water gas shift reaction, various oxidation and hydrolysis reactions [1]. Although their catalytic properties are, in some cases, as good as those of their homogeneous counterparts (and sometimes even better), so far none, to our knowledge, has had any industrial application. This is correlated to the frequent observation of significant metal leaching, a problem which is in many cases directly related to the catalytic reaction investigated. Thus, for example, an anchored Wilkinson type catalyst $(\mathrm{RhCl(PR_3)_2(PR_2}\approx\mathrm{OSi}\equiv)$ will not be stable, under the conditions of hydrogenation or hydroformylation of olefins towards metal bleeding because the mechanism of this reaction implies a step of decoordination of a phosphine ligand to allow for the coordination of the entering olefin. A high surface concentration of anchored phosphines and a low ratio [[metal]/[ligand] were recommended either to allow for the coordination of two neighbouring phosphines, so as to stabilize the complex via a chelate effect, or to favor the recoordination of a surface phosphine during the catalytic cycle. Alternatively, it seems that, in this precise case, one must simply reconsider the method of immobilization of the metal complex, and choose one which is better adapted to the target reaction (see, for example, the sol-gel procedures)

2.2. *Encapsulated, intercalated or entrapped catalysts*

The objective, clearly, is to improve the stability of the metal complex under the reaction conditions by preventing the catalytic species from dimerizing or aggregation, and to tune the selectivity of the reaction using the walls of the pores of the solid via steric effects. The encapsulation of transition metal complexes in inorganic solids was mainly performed by three methods. Two of them introduce (or synthesize) the complex inside the porous network of a pre-formed solid either by encapsulation or by intercalation; the third one uses the complex as one of the reactants in the mixture of synthesis of the solid: the complex is, thus, entrapped inside the pores.

2.2.1. Encapsulated catalysts

In this approach, the metal is introduced in the pores of a solid (mostly large pore zeolites) either via cation exchange or as a complex labile towards ligand substitution. The ligands [CO, PR_3, 1,2-dicyanobenzene, *N*,*N*′-bis(salicylidene)ethylene diamine (H_2Salen) and more recently 5,7,12,14-tetramethyl-1,4,8, 11-tetraazacyclotetradeca-4,6,11,13-tetraene (TMC)] are then introduced under the conditions of complex formation. The first examples have concerned metal carbonyl clusters, such as $Rh_6(CO)_{16}$, $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$ which were synthesized inside the large pores of zeolites such as HY, NaY or 13X [13,14]. In contrast to those supported on nonporous inorganic oxides, the zeolite entrapped carbonyl clusters are stable toward oxidation–reduction cycles. As carbonyl clusters are not among the most active known catalysts, because they are saturated entities, their interest resides essentially in more fundamental aspects of catalysis [14]. At high temperature, under vacuum or reducing conditions (such as CO, H_2), these metal carbonyl clusters aggregate to small metal particles, whose size is restricted by the dimensions of the zeolitic framework. For a number of catalytic reactions, the size of the pores controls the size of the products formed; thus a higher selectivity to the lower hydrocarbons has been reported for the Fischer Tropsch reaction.

The strong similarity of zeolites with the protein portion of natural enzymes was emphasized by Herron [15]. The protein protects the active site from side reactions, sieves the substrate molecules and provides a stereochemical demanding void. These remarks induced research in the field of metal complexes encapsulated in zeolites which would mimic these metalloenzymes for oxidation reactions. Two types of complexes were essentially used, the Salen and the phtalocyanine (Pc) complexes; their dimensions fit that of the large pores of available zeolites. The number of such zeolites is very limited (Fig. 1). Thus, the aluminosilicate Faujasite (X, Y, EMT)

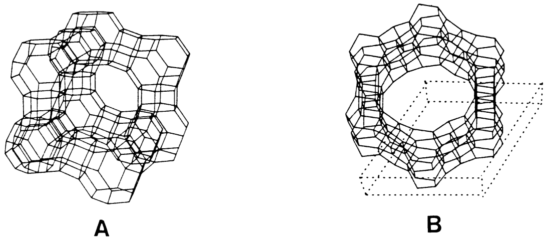
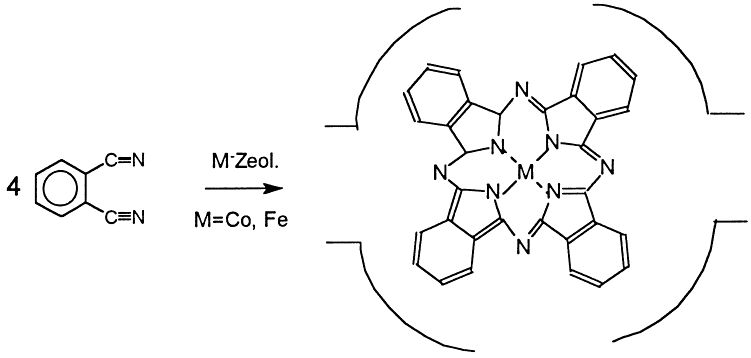
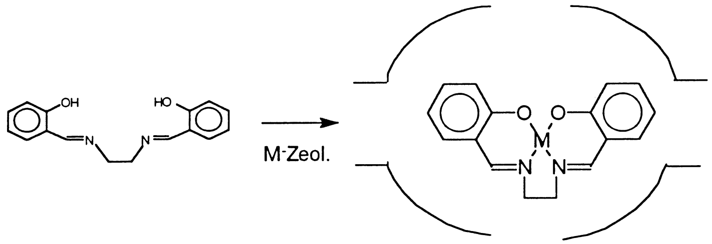


Fig. 1. Structures of (a): Faujasite (zeolite Y), framework viewed along [111], pore diameter: 7.4 Å; and (b): VFI (VPI-5), framework viewed along [001], pore diameter; 12.1 Å [147].



Scheme 5. Synthesis of encapsulated phtalocyanine complexes.



Scheme 6. Ship-in-the-bottle synthesis of encapsulated Salen complexes.

encapsulates Rh(III)Salen, Co(II)Salen, Mn(Salen)$^+$, Pd(Salen), Fe(II)Pc, CoPc and FeTMC [16–23]. The aluminophosphate VPI-5 is able to accomodate FePc [24].

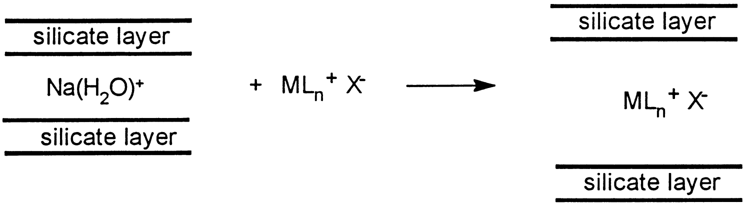
The ligand 1,2-dicyanobenzene enters easily the pores of these two zeolites; the large ligand H_2Salen and the macrocycle TMC are flexible enough to enter these pores (Schemes 5 and 6).

In both cases, the complex formed is like a "ship-in-a-bottle", confined in the super cages of the zeolite: this explains the reported greater stability of these catalysts as compared with the same complexes in solution. No metal leaching is observed, as long as the complex is exclusively inside the pores.

For all reactions tested, i.e. oxidation of alkanes or alkenes, hydrogenation of alkenes, and for all such encapsulated catalysts, a high selectivity in competitive reactions is observed, which is correlated to molecular sieving effects (reactants size selectivity effect), and a better regioselectivity is obtained (the 2 position favored over the 4 position in the oxidation of *n*-octane, for example) [16,18,19,25]. These good selectivities are associated, as expected, with lower activities due to more or less severe diffusion limitations.

2.2.2. Intercalated catalysts

This method introduces the cationic catalyst as such between the silicate layers of swelling clays, such as smectites, by the conventional ion exchange procedure (Scheme 7).



Scheme 7. Synthesis of intercalated complexes.

Thus, complexes such as $Rh(NBD)(PPh_3)_2^+$ (NBD: norbornadiene) or $Rh(DPPE)(NBD)^+$, (DPPE = 1,2-bis(diphenyldiphosphino)ethane), Rh(COD)-(S)-BINAP)$^+$ and Rh(COD)[(S)-(R)-BPPFA)]$^+$(COD: cyclooctadiene) were intercalated in hectorite [26–28]. In all cases, an increase of the interlayer spacing, as determined by XRD, strongly suggests that a true intercalation occurred. These catalysts were tested for various reactions of hydrogenation of alkenes and alkynes, of asymmetric hydrogenation of α,β-unsaturated carboxylic acid esters. A strong solvent effect is generally observed, which correlates to their swelling efficiency. The differences in selectivies as compared with those of their homogeneous analogs reflect steric effects, but also surface chemical effects. In the case of asymmetric catalysis [28], the dependence of the selectivity on the solvent and bulkiness of the ester group suggests that the interaction between the substrate and the active site increases in the interlayer space, thus enhancing the enantioselectivity. But, problems of metal leaching are not fully solved, so that in some cases, the functionalization of the interlayer and the utilization of the methods described by eq. 4 are recommended [29]. Because the size of the interlayers can be easily adjusted by incorporation of complex moieties of different sizes, these clays (montmorillonites, hectorites etc.) may, nevertheless, compete with zeolites, which have a rigid, predetermined size.

2.2.3. Entrapped catalysts

In this approach, the metal complex is introduced directly in the mixture of reactants used for the synthesis of the solid support. Work in this area was pioneered by Panster et al. [30]. Thus, for example, the sol-gel processing of the functionalized complexes, $(RO)_3Si\sim L'ML_n$ leads to a solid with homogeneously distributed metal entities through the whole material. The catalyst is entrapped in the solid, but as porosity and surface area can be easily tuned, access of the reactants to the metal center is possible. A detailed study of the catalytic properties of Wilkinson type catalysts, homogeneous or heterogenized by different methods, shows that the sol-gel processed catalysts show similar activities (example concerns the hydrosilylation of 1-hexene by triphenylsilane), but that they are definitely much more stable [31]. A number of other entrapped complexes as well as their sulfonated analogs and their quaternary ammonium salts have already been prepared by this procedure and successfully tested for reactions such as isomerization, hydrogenation and hydroformylation of olefins, hydrogenation of α,β-unsaturated olefins; the results all confirm the superior stability of these latter catalysts, and their reasonable activities if one considers that all catalytic centers are not accessible [28,31–34].

Similarly, metal complexes can be introduced among the reactants for the hydrothermal synthesis of zeolites; they will thus be entrapped in the porous network of the zeolite [35].

In conclusion, the problems encountered with encaged complexes clearly show the importance of finding new porous solids, able to accommodate the metal complexes of interest and allow for the diffusion of reactants and products. The synthesis of a novel family of mesoporous silicoaluminates, MCM-41 and HMS [36–38], with pore diameters comprised between 20 and 100 Å, tunable via the size of the template used for the synthesis, seems promising. But, given their structure (straight monodimensional channels) metal complexes cannot be encapsulated, so that the inner surface must be functionalized exactly as any inorganic oxide [39,40]. But, one can expect to obtain good selectivities by the simultaneous choice of the metal complex, the size of the substrate and the pore diameter.

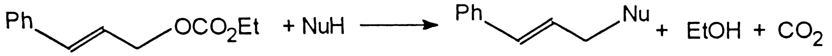
2.3. *Supported liquid phase catalysts*

Catalysis in biphasic media is one of the most elegant and efficient ways to solve the problem of catalyst recovery. Many excellent reviews are available and industrial processes are currently running [41–45]. This method is, as all others, not applicable for all situations, and particularly when the solubility of the reactants in the catalyst phase is too low: then the activity is correlated to the interfacial surface, which is small. In these cases, supporting the catalyst in a thin film of liquid deposited on a solid of high specific surface area improves significantly the activity.

The synthesis of supported liquid phase catalysts was described for the first time in 1939 [46]. Their domain of application and a first description of their mode of operation were later reported simultaneously by Acres et al. [47] and by Rony [48,49]. The method, inspired from gas liquid chromatography, uses a catalyst deposited on the surface of a high surface area porous inorganic oxide in a thin film of a non volatile solvent; reactants and products are in the gas phase. This technique was applied for the isomerization of pentene-1 catalyzed by $RhCl_3$ (in a film of ethylene glycol) and to the hydroformylation of propene catalyzed by $(Ph_3P)_2Rh(CO)Cl$ (in a film of benzylbutylphtalate). The amount of solvent must be large enough to constitute a small film on the solid, but low enough to avoid pore plugging, that restricts diffusion of the reactants. The phosphine itself, molten under the reaction conditions, can serve as solvent [50–53]. This method seemed to be suitable only for gaseous reactants and products since the presence of flowing organic liquids can draw the supported liquid out of the system. High temperatures of reaction are, thus, needed which can also bring about the volatilization of the solvent involved in the liquid phase catalysts. To avoid this, membrane reactors were employed [54].

Renewed interest for this type of method came recently from its adaptation to the immobilization of water/organic solvent biphasic catalysts, resulting in the so-called supported aqueous phase catalysts (SAPC) [55]. The molecular catalyst is immobilized via water, hydrogen bonded to the surface silanol groups; reactants and products are in the organic phase (Scheme 1). Thus, HRh(CO)(tppts)$_3$/H_2O/silica (tppts = sodium salt of tri(*m*-sulfophenyl)phosphine) catalyzes the hydroformylation of heavy and functionalized olefins, [56–60] the selective hydrogenation of α,β unsaturated aldehydes [34] and the asymmetric hydrogenation of 2-(6′-methoxy-2′-naphtyl) acrylic acid, a precursor of naproxen [61–63]. More recently, this methodology was tested for the palladium catalyzed reactions of Trost-Tsuji (allylic substitution) and of Heck (olefin arylation) [64,65].

In most cases, the SAP catalysts are less active than their homogeneous counterparts, but more active than their liquid biphasic catalyst, a phenomenon very simply interpreted as the result of the increase of the interphase surface area which in the case of the SAP catalysts is close to that of the silica support. This is illustrated by the results obtained with the system Pd(OAc)$_2$/5tppts under biphasic or SAP conditions for the reaction of allylic substitution (eq. 10) and given in Table 1 [66].



NuH: ethyl acetoacetate, morpholine (10)

With CH_3CN as a solvent, the SAP catalysts show an activity lower than the biphasic system, independently of the water content of the solid and of the nature of the nucleophile; this must be correlated to total miscibility of H_2O and CH_3CN. With ethylacetoacetate, the SAP catalyst is highly selective in accordance with the low water concentration (in H_2O/CH_3CN, cinnamyl alcohol forms).

With PhCN as a solvent, the SAP catalyst is superior to its truly biphasic analog for both nucleophiles, whatever its water content; maximum activity of the SAP catalyst is observed with water contents close to approximately 50 wt.% H_2O (which is close to that necessary to fill the pores of the silica support). Finally, the SAP catalyst is, in all cases, more stable towards degradation to metallic particles.

The SAP methodology is still in its infancy and although the importance of the

Table 1
Catalytic properties of Pd(OAc)$_2$/5tppts in H_2O/nitrile (1/1) and under SAP conditions [66]

Nucleophile	Solvent	Catalyst type	*T* (°C)	Conv. (%)	Sel.(%)[d]
Ethylacetoacetate	CH_3CN	biphasic	80	50[a]	50[e]
	CH_3CN	SAP (22% H_2O)	80	40[a]	95
	PhCN	biphasic	80	0[b]	
	PhCN	SAP (32% H_2O)	80	90[b]	95[f]
Morpholine	CH_3CN	biphasic	50	85[c]	100
	CH_3CN	SAP(50% H_2O)	50	30[c]	100
	PhCN	biphasic	50	5[c]	100
	PhCN	SAP (50% H_2O)	50	95[c]	100

[a] After 8 h; [b] after 40 min; [c] after 5 min.

[d] For the monoalkylated product; [e] cinnamyl alcohol formed; [f] dialkylated product formed. SAP catalyst is supported on a mesoporous (pore ∅: 24 nm) silica from Grace.

water amount of the solid has been stressed by all authors, a complete evaluation of the catalytic behavior has not yet been performed: kinetic data, recycling tests, determination of the level of metal leaching and of the possible water loss into the organic solvent must be properly determined before any industrial application can be safely considered. Presently, the range of potential applications is widely open, as only very few substrates, reactions, solid supports, polar or non volatile solvents were tested.

3. Heterogeneous molecular catalysts

As we defined in the Introduction, we will distinguish two types of heterogeneous molecular catalysts: (1) those which are synthesized from an organometallic complex by its reaction with the surface of an oxide: the grafted complex is precisely the catalyst or the catalyst precursor (heterogeneous organometallic catalysts); (2) those which use an organometallic complex only to introduce the metal site on a surface; the labile ligands of the grafted complex are then replaced by ligands adapted to the target reaction in accordance with known homogenous or heterogeneous catalysts (heterogeneous molecular catalysts).

3.1. Heterogeneous organometallic catalysts

Most of the complexes which were heterogeneized "intact" have in their coordination sphere mainly "soft" ligands; a direct bonding between the metal and the functional groups present on the surface of inorganic oxides, introduces "hard" ligands in the first coordination sphere of the metal. This will generally lead to important changes in the chemical and catalytical properties.

3.1.1. From metal carbonyl clusters

The anchoring of metal carbonyl clusters on inorganic oxides was studied very extensively in the 1980s with many different objectives, most of them directly related to the structure of these complexes. Indeed, the presence of bonds between metal atoms in their zero oxidation state has lead to the assumption that these complexes might mimic small metal particles, covered with carbon monoxide [67,68]. This latter hypothesis was not verified, but complexes such as $M_3(CO)_{12}$ $M=Os$, Ru, $M_4(CO)_{12}$ (M: Co, Ir) or $Rh_6(CO)_{16}$ were shown to be excellent precursors of small metallic particles [14]. The small size seems to be related to the preexistence of the metal in its zero oxidation state; this avoids a reduction step under severe conditions, which generally favor sintering. This is also the supposed origin of some of the differences in the catalytic properties of particles synthesized using these precursors [14].

The reactivity of a metal carbonyl cluster and the surface of inorganic oxides is now well known. Table 2 shows some of the reactions which were evidenced; they are those well known in molecular organometallic chemistry. It is then clear that,

Table 2
Some of the types of surface reactions between an organometallic complex and an inorganic oxide

Surface sites	Type of reaction	Examples	Ref.
Bronsted acid	Electrophilic attack	$SnR_4 + \equiv SiOH \rightarrow \equiv SiOSnR_3 + RH$	[69]
	Oxidative addition	$Ru_3(CO)_{12} + \equiv SiOH \rightarrow (\equiv SiO)(H)Ru_3(CO)_{10} + 2CO$	[70]
	Protonation of a M≡C bond	$X_3W \equiv CCMe_3 + \equiv SiOH \rightarrow (\equiv SiO)X_3W = CHCMe_3$	[71,72]
Bronsted base	Nucleophilic attack on a coordinated CO	$Fe_3(CO)_{12} + =AlOH \rightarrow =Al^+[HFe_3(CO)_{11}]^-$	[73]
	Hydride abstraction	$H_2FeOs_3(CO)_{13} + \text{-}MgOH \rightarrow [HFeOs_3(CO)_{13}]^- 1/2Mg^{2+}$	[74]
	Disproportionation	$Co_2(CO)_8 + –MgOH \rightarrow Co^{2+} + [Co(CO)_4^-]_2Mg^{2+}$	[75]
Lewis acid	Formation of a tight ion pair	$(CO)_4Co^-–Mg^{2+}–Co(CO)_4^-$	[75]
Lewis base	Nucleophilic attack on a coordinated CO	$Fe(CO)_5 + Mg^{2+}O^{2-} \rightarrow [(CO)_4Fe(CO_2)]^- Mg^+$	[76]

now, one should be able to predict the nature of the surface complex formed by reaction of any organometallic complex with any inorganic oxide.

Most of the resulting anchored complexes do not show exceptional catalytic properties: they were tested for a number of reactions, such as CO hydrogenation [77], water gas shift [78], but the most soundly proven catalysis by metal carbonyl clusters concerns hydrogenation of ethylene [79,80] and isomerization of olefins [81,82]. Catalysis by such metal carbonyl clusters does not seem to have any future industrial application: these supported carbonyl clusters are either very unstable towards degradation under reaction conditions or are so stable that they are almost inactive.

In our opinion, the main interest of these studies resides in the fact that they allowed a good rationalization of the surface chemistry of a number of inorganic oxides. In particular, methods were developed to determine accurately the nature of the surface functional groups present on the most common supports used for heterogeneous catalysis (silica, alumina, silica–alumina, magnesia) and their concentration as a function of their pretreatments [83–93]. The most studied system was undoubtedly $Os_3(CO)_{12}/SiO_2$, for which the anchoring reaction is an oxidative addition of surface silanols across an Os–Os bond, which results in the formation of the surface complex $(\equiv SiO)(H)Os_3(CO)_{10}$: (eq. 11)

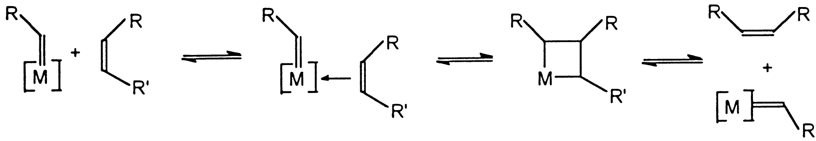
$$Os_3(CO)_{12} + \equiv SiOH \rightarrow (\equiv SiO)(H)Os_3(CO)_{10} + 2CO \tag{11}$$

A large battery of techniques were used to prove the occurrence of this reaction and the precise structure of the anchored cluster: IR [94–96], Raman [97] and MAS NMR [98] spectroscopies, quantitative volumetric measurements, EXAFS, [99,100] synthesis of molecular analogs such as $(Et_3SiO)(H)Os_3(CO)_{10}$ [101] and computer modelling [102,103].

It is now admitted that the reactivity of organometallic complexes towards inorganic oxides closely parallels the related solution organometallic chemistry (same type of reactions), but owing to the rigidity of the surface of the solids, consecutive reactions are less numerous or even suppressed. This property was used in different ways. It allowed the clean synthesis of some large metal carbonyl clusters, difficult to obtain in a pure form by solution reactions [104–106]. It allowed the design of anchored catalysts for a given target reaction; the knowledge of the surface chemistry and of the mechanisms of homogeneous (and/or heterogeneous) catalysis leads to the choice of the best couple complex/support. We will give two examples which show the potential of this latter approach, but also some of the difficulties which are still encountered.

3.1.2. From alkyl and alkylidyne complexes

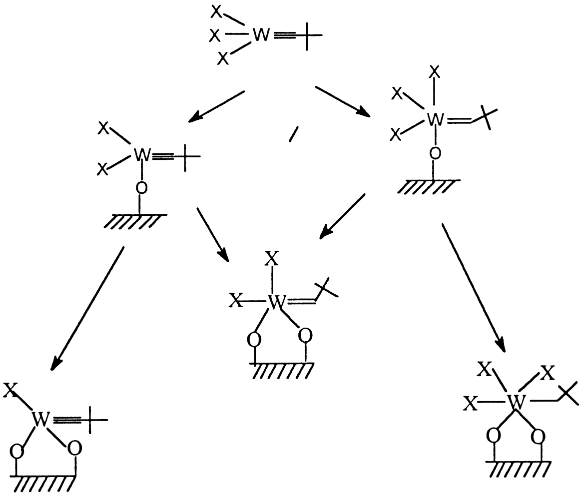
3.1.2.1. For the metathesis of olefins. In heterogeneous catalysis, the most active catalyst is Re_2O_7/Al_2O_3 with or without an alkylating agent such as SnR_4, but the precise nature of the active site is still a matter of debate [107–111]. In homogeneous catalysis, most active homogeneous catalysts now incorporate a metallocarbene [112–116] or a metallacycle [117,118] and the mechanism generally admitted is the metallocarbene mechanism of Chauvin [119,120]: (eq. 12)



(12)

Based on these data, the synthesis of heterogeneous molecular catalysts was attempted using as precursor complexes CH_3ReO_3 and $X_3W{\equiv}CCMe_3$ (X = Np, Cl), respectively. The first complex, CH_3ReO_3, inactive towards metathesis of olefins, becomes active when chemisorbed on alumina, silica–alumina [121], or on niobia [72]. The latter support leads to the most efficient catalyst. A correlation between catalytic activity and Lewis acidity of niobia was observed and the presence of the methyl fragment was demonstrated; but at least three different methylrhenium surface complexes are present on the surface, as suggested by ^{13}C MAS NMR data. Finally, the formation of 3-methyl-butene-1, but also of 2,4-dimethyl-2-pentene, probably 5-methyl-2-hexene and isobutene by the stoichiometric reaction of trans-2,5-dimethyl-hexene-3 suggests the occurrence of an intermediate π-allyl species, correlated to the partial reduction of the initial Re^{VII} complex to Re^{V} [122]. Therefore, the catalyst cannot be considered as a well-defined heterogeneous molecular catalyst and the observed activity reflects the variety of surface complexes formed from CH_3ReO_3. Finally, the presence of the expected methylidene complex $[Re]_s{=}CH_2$ could not be confirmed. This study clearly shows that although the precursor complex is rather simple, its reactivity is complicate with a surface like niobia, which possesses both Bronstedt and Lewis surface sites able to react with either the Re–C bond or the Re$=$O bond, a reactivity difficult to control.

In the case of $X_3W{\equiv}CCMe_3$ ($X=Cl$, Np), one expects that the major reaction would be the addition of a surface hydroxyl group on the carbynic bond which leads to the expected neopentylidenetungsten surface complex. In this case also, a complete study with niobia as support evidences many surface reactions, whose relative importance is function of the pretreatment [123] (Scheme 8).



Scheme 8. Some of the possible reactions between the surface of niobia and the complex $X_3W{\equiv}CCMe_3$.

Thus, because there are different ligands around the metal center, which all are reactive with the surface functional groups under very similar conditions, we obtain an active catalyst for the metathesis of olefins, but yet far from being clearly identified. One faces, thus, the same difficulties as with traditional heterogeneous catalysts.

These examples clearly show that the formation of only one type of surface species needs the use, as precursor species, of a complex in which the metal center bears only one type of ligands, susceptible to react with only one type of surface functional groups. The synthesis of Zr-based molecular catalysts illustrates perfectly this concept.

3.1.2.2. For the hydrogenolysis of alkanes and the dehydrocoupling of silanes. Among the organometallic complexes able to perform these two reactions, one finds alkyl and hydride d° complexes of early transition metals and lanthanides [124–131]. For both reactions, the electrophilicity of the metal is an important parameter which influences the first step of the catalytic cycles, i.e. the C–H and the Si–H bond activation:

$$[M]-H+{\equiv}C-H\rightarrow[M]-C{\equiv}+H_2 \tag{13}$$

$$[M]-H+{\equiv}Si-H\rightarrow[M]-Si{\equiv}+H_2. \tag{14}$$

Dimerization of the active [M]–H entity is one of the generally admitted deactivation processes. It was shown [132–134] and recently confirmed [135–137] that it is possible to synthesize very electrophilic and thermally stable zirconium hydrides anchored on the surface of silica, starting from the homoleptic tetraneopentylzirconium, $ZrNp_4$, and the surface of a silica. The first reaction is a protonolysis of the alkyl complex by the surface silanol groups, the second one is a hydrogenolysis reaction: (eqs. 15–16)

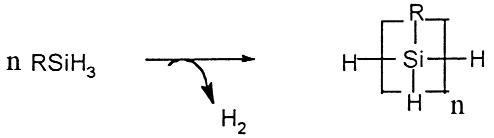
$$ZrNp_4 + \equiv Si\text{-}OH \rightarrow \underset{(\mathbf{1})}{\equiv Si\text{-}OZrNp_3} + NpH \qquad (15)$$

$$\underset{(\mathbf{1})}{\equiv Si\text{-}OZrNp_3} + H_2 \rightarrow \underset{(\mathbf{2})}{(\equiv Si\text{-}O)_{4\text{-}x}ZrH_x} + 9CH_4 + 3C_2H_6\ ,\ x=1, 2. \qquad (16)$$

By choosing a silica with only isolated surface silanol groups (i.e. dehydroxylated at 500 °C under vacuum) and by using a substoichiometric amount of $ZrNp_4$, one restricts the reaction to the formation of the trisneopentylsurface complex (**1**) and a good dispersion of the related zirconium hydride species. Moreover, the reaction of this complex with the surface leads to the liberation of neopentane, a molecule totally inert towards the surface; this avoids the subsequent reactions often encountered with other precursors such as chlorides, for example.

The supported zirconium hydrides hydrogenolyze alkanes [138] (eq. 17, Fig. 2) and polymerize silanes [139] (eq. 18, Fig. 3), both under mild conditions: (eqs. 17–18)

$$C(CH_3)_4 + H_2 \rightarrow (CH_3)_2CHCH_3 + CH_4 \rightarrow \ldots \rightarrow C_2H_6 + 3CH_4 \qquad (17)$$



$$n\ RSiH_3 \xrightarrow[H_2]{} H\!-\!\left[\begin{array}{c} R \\ | \\ Si \\ | \\ H \end{array}\right]_n\!-\!H \qquad (18)$$

For the catalytic dehydrogenative coupling of silanes, the performances of these $[Zr]_s$–H complexes are quite different from those observed with homogeneous zirconium hydride complexes [140]; thus, all types of silanes are activated (primary, secondary and even tertiary) and the rate of polymerization is higher. Finally, for some silanes, such as Et_3SiH for example, both Si–H and C–H bonds are activated [139]. Alkane hydrogenolysis was never reported with homogeneous zirconium hydrides, but one can reasonably think that methane would not be activated by these latter complexes, because of the temperature needed (150 °C), a temperature well above the domain of stability of these complexes. The outstanding properties of the silica supported zirconium hydride complexes seem to be correlated to the "solid" ligand, through electronic and/or immobilizing effects. Formally an eight e^- species, the surface zirconium hydrides are highly electron deficient entities when compared with the 16 e^- cyclopentadienyl stabilized molecular complexes.

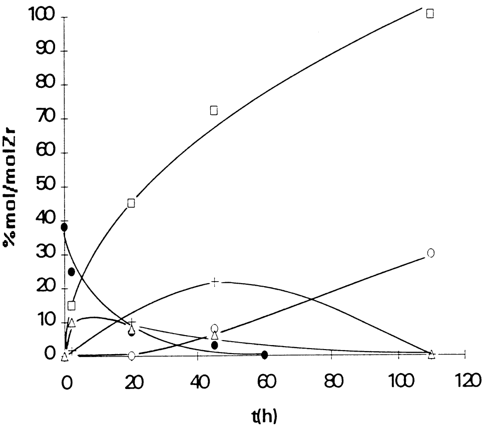


Fig. 2. Hydrogenolysis of neopentane at 100 °C catalyzed by ($\equiv$SiO)$_3$ZrH. Evolution of the composition of the gas phase as a function of time ($p_{\mathrm{NpH}}=40$ Torr, $p_{\mathrm{H2}}=200$ Torr); □ methane; ○ ethane; + propane; △ isobutane; ● neopentane.

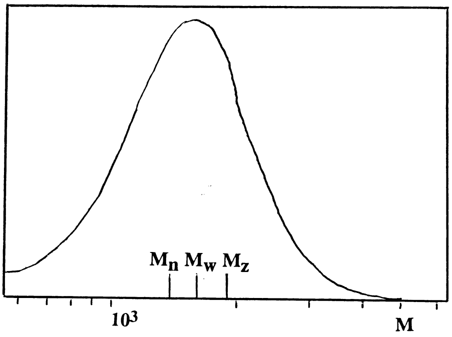


Fig. 3. Mass distribution of the polysilanes obtained by dehydrocoupling of *n*-hexylsilane catalyzed by ($\equiv$SiO)$_3$ZrH, as determined by SEC (calibrated against polystyrene).

Immobilization of these hydrides on a solid surface also accounts for their remarkable stability toward temperature (up to 200 °C) and dimerization [137].

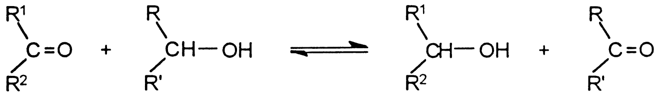
3.2. Heterogeneous molecularly dispersed catalysts

The poor selectivity of heterogeneous catalysts (supported metals or oxides) is often correlated to the presence of numerous types of potentially active sites on the surface of the solid, the metal center being in various chemically, electronically and/or structurally environments. When the target reaction needs isolated sites, then again the organometallic approach must be considered. We will illustrate this approach with two examples taken from our work on Zr-based catalysts: they concern the reactions of hydrogen transfer between ketones and secondary alcohols

(Meerwein–Ponndorf–Verley reduction and Oppenauer oxidation) and epoxidation of olefins by H_2O_2.

3.2.1. *For the hydrogen transfer between ketones and alcohols (MPVO reactions)*

The hydrogen transfer reaction between ketones and secondary alcohols (eq. 19) is catalyzed inter alia in the homogeneous phase by group 4 metal alkoxides, $M(OR)_4$. [141]



$$R^1R^2C{=}O + RR'CH{-}OH \rightleftharpoons R^1R^2CH{-}OH + RR'C{=}O \qquad (19)$$

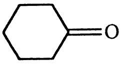
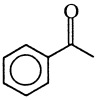
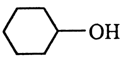
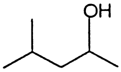
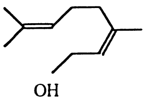
The deactivation of these homogeneous catalysts is generally explained by their extensive self association, via alkoxy bridges. With bulky ligands self association is restricted, but access of the reactants to the metal center is more difficult, hampering the observation of good activities. We have recently shown that controlled alcoholysis with isopropanol of the supported complex $(\equiv SiO)ZrNp_3$ leads (eq. 20) to the related supported Zr isopropoxy complex, $(\equiv SiO)Zr(Oi{-}Pr)_3$, an active and recyclable catalyst for the MPVO reaction [142].

$$\underset{(1)}{(\equiv SiO)ZrNp_3} + 3i-PrOH \rightarrow \underset{(3)}{(\equiv SiO)Zr(Oi-Pr)_3} + 3NpH \qquad (20)$$

Table 3 illustrates some of the properties of this heterogeneous molecular catalyst.

Several points warrant comment: (i) the supported complex is an active catalyst for both Meerwein–Ponndorf–Verley and Oppenauer reactions, the reactivities of

Table 3
Catalytic properties of $(\equiv SiO)Zr(OiPr)_3$ for the reactions of hydrogen transfer between ketones and alcohols

Substrate	Reductant (oxidant)	[substrate]/[Zr]	T (K)	% Conv.
	*i*PrOH[a]	72	353	75[c]
	*i*PrOH[a]	50	353	38[c]
	PhC(O)Me	40	383	49[b]
	PhC(O)Me	40	383	55[d]
	PhCHO	72	383	49[b]

[a]Solvent: iPrOH. [b]After 6 h, solvent: toluene. [c]After 20 h. [d]Solvent: octane.

the different substrates being explained by steric and/or electronic effects, and by the relative stability of the intermediate alkoxyzirconium complexes towards alcohols; (ii) $Zr(OiPr)_4$ under the same experimental conditions is totally inactive, a fact which must be correlated to its self association; (iii) this supported Zr complex is more active than the silica supported Zr catalyst obtained from $Zr(OiPr)_4$ [143]; (iv) no Zr leaching was detected and this catalyst can be recycled without significant loss of activity by simple filtration and in some cases regeneration with boiling isopropanol.

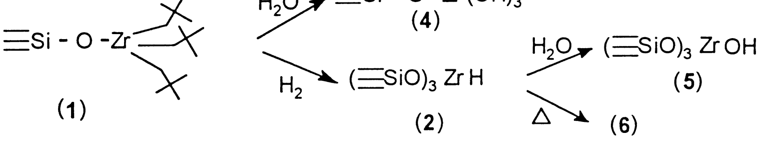
These observations strongly suggest that this silica supported tris(isopropoxy)–zirconium complex is a true mononuclear complex, self association being avoided by an initial good dispersion of Zr on the silica surface (silica was partially dehydroxylated so as to have only isolated surface silanols, and a low Zr loading was used) and by the stability of the $Zr–[O]_s$ bond under the reaction conditions.

3.2.2. *For the epoxidation of olefins by H_2O_2*

The best heterogeneous catalyst for the epoxidation of olefins, using aqueous H_2O_2 as oxidant, is presently the ENICHEM catalyst, a titanosilicalite, TS-1 [144]; in this solid, the titanium, which is substituted for silicium in the framework of silicalite, is perfectly isolated (no Ti–O–Ti bonds). This structural property is considered as the key parameter of the high selectivity for epoxide formation. But this catalyst is not accessible to large molecules (pore size: 5.6 Å), so that the search for a non-microporous catalyst, stable in presence of water, is still a challenge. Three zirconium-based solids were synthesized, as shown in Scheme 9.

Complexes (**4**) and (**5**) differ by the number of surface anchoring bonds. Surface complex (**6**) is not yet fully identified: it is tentatively considered as either a surface zirconyl species $(\equiv SiO)_2Zr=O$ or a tetraasiloxyzirconium, $(\equiv SiO)_4Zr$ [145].

The results of the tests of oxidation of cyclohexene with H_2O_2 (Table 4) are very surprising for several reasons: (i) Zr-based catalysts are reportedly poor catalysts in the homogeneous or heterogeneous phase [146]. The activity of these supported catalysts compares with that of conventional amorphous titanium-based solids: total epoxidation yields (including diol) are close to 55%. (ii) No metal leaching into the solution could be detected. (iii) Differences in terms of activity per Zr_s and of selectivity are observed between the three solids, which seem to be correlated to the structure of the precursor surface entity, but may also be a function of Zr concentration, a factor which may govern the extent of site isolation.



Scheme 9. Synthesis of heterogeneous molecular zirconium based catalysts [145].

Table 4
Catalytic properties of Zr-based molecular heterogeneous catalysts for the epoxidation of cyclohexene with H_2O_2

Catalyst	Zr (wt.%)	H_2O_2 conv. (%)	Select. (%)		Tot. select. (%)
			Epoxide	Diol	
4	0.93	76	63	8	71
5	0.67	68	59	6	65
6	0.37	72	70	5	75

4. Conclusions and perspectives

This short overview highlights the many possibilities which are already available to synthesize well-defined and efficient heterogeneous molecular catalysts for a given target reaction. The approaches are as numerous as are the reactions one can envisage. Many others are emerging using dendrimers, mixed solids such as films of polymers on the surface of inorganic oxides, nanotubes of carbon, mesoporous solids etc. There is a clear demand for such catalysts, but this supposes that these new molecular heterogeneous catalytic systems are simultaneously well characterized, efficient and stable for the target reaction. Most studies still concentrate only on one of these aspects; thus, the literature is full of examples of very nice systems, characterized after considerable effort, which appeared to be uninteresting catalysts, while excellent catalysts are described by a crude hypothetical scheme. It is our opinion that the design of an heterogeneized molecular catalyst or of an heterogeneous molecular catalyst must incorporate, at first, all the available data from solid-state and organometallic chemistries, from heterogeneous and homogeneous catalysis, but also the parameters of the target reaction. These latter include not only the precise nature of the reactants, but also of the main and secondary reaction products, the solvent and the experimental reaction conditions (temperature, pressure etc.). Although some of the causes of metal leaching, one of the major drawbacks of this type of catalysts, can be easily suppressed by choosing the proper precursor complex and method of immobilization, it appears that the reactivity, and thus the stability, of the anchoring bonds are still almost unknown.

However, even when following such a rigorous methodology, much room is left for the imagination and innovation. The chances of success will certainly rely on a better cooperation between specialists in the fields of polymers, inorganic solids, organometallic complexes, organic chemistry and catalysis.

References

[1] F.R. Hartley, Supported Metal Complexes, D. Reidel, Dordrecht, 1985.
[2] W.T. Ford (Ed.), Polymeric Reagents and Catalysts, American. Chem. Soc., Washington, DC, 1986.
[3] D.C. Sherrington, P. Hodge (Eds.), Syntheses and Separations using Functionnal Polymers, Wiley, Chichester, 1988.

[4] D.C. Sherrington, Pure Appl. Chem. 60 (1988) 401.
[5] D.E. Bergbreiter, J.R. Blanton, R. Chandran, M.D. Hein, K.J. Huang, D.R. Treadwell, S.A. Walker, J. Polym. Sci., Polym. Chem. Ed. 27 (1989) 4205.
[6] P. Hodge, Polymer supported asymmetric organic synthesis, in: R. Epton (Ed.), Innovation and Perspectives in Solid Phase Synthesis, SPCC UK, 1990, p. 273.
[7] D.C. Sherrington, Polymer supported synthesis, in: J.H. Clark (Ed.), Chemistry of Waste Minimization, ch. 6, Blackie, 1995, p. 141.
[8] W.O. Haag, D.D. Whitehurst, German Patent 1 800 371, 1969.
[9] K.D. Behringer, J. Blümel, Inorg. Chem. 35 (1996) 1814.
[10] K.D. Behringer, J. Blümel, Chem. Commun. (1996) 653.
[11] U. Nagel, E. Kinzel, J. Chem. Soc., Chem. Commun. (1986) 1098.
[12] B. Pugin, M. Müller, Stud. Surf. Sci. Catal. 78 (1993) 107.
[13] E. Montavani, N. Palladirio, A. Zanotti, J. Mol. Catal. 3 (1977) 385.
[14] M. Ichikawa, Adv. Catal. 38 (1992) 283.
[15] N. Herron, Chem. Tech. (1989) 542.
[16] K.J. Balkus, Jr, A.A. Welch, B.E. Guade, Zeolites 10 (1990) 722.
[17] N. Herron, Inorg. Chem. 25 (1986) 4714.
[18] C. Bowers, P. Dutta, J. Catal. 122 (1990) 271.
[19] S. Kowalak, R.C. Weiss, K.J. Balkus Jr., J. Chem. Soc., Chem. Commun. (1991) 57.
[20] N. Herron, G.D. Stucky, C.A. Tolman, J. Chem. Soc., Chem. Commun. (1986) 1521.
[21] F. Thibault-Starzyk, R.F. Parton, P.A. Jacobs, Stud. Surf. Sci. Catal. 84 (1994) 1419.
[22] S. Ernst, Y. Traa, U. Deeg, Stud. Surf. Sci. Catal. 84 (1994) 925.
[23] J.C. Medina, N. Gabriunas, A. Paez-Mozo, J. Mol. Catal. 115 (1997) 233.
[24] R.F. Parton, C.P. Bezoukhanova, F. Thibault-Starzyk, R.A. Reynders, P.J. Grobet, P.A. Jacobs, Stud. Surf. Sci. Catal. 84 (1994) 813.
[25] F. Bedioui, E. De Boysson, J. Devynck, K.J. Balkus, Jr, J. Chem. Soc. Faraday Trans. 87 (1991) 3831.
[26] T.J. Pinnavaia, R. Raythatha, J. Guo-Shuh, L.J. Halloran, J.F. Hoffman, J. Am. Chem. Soc. 101 (1979) 6831.
[27] R. Raythatha, T.J. Pinnavaia, J. Catal. 80 (1983) 47.
[28] J. Blum, A. Rosenfeld, N. Polak, O. Israelson, H. Schumann, D. Avnir, J. Mol. Catal. A: Chem. 107 (1996) 217.
[29] B.M. Choudary, K. Ravi Kumar, M. Laksimi Kantam, J. Catal. 130 (1991) 41.
[30] U. Deschler, P. Kleinschmitt, P. Panster, Angew. Chem. Int. Ed. Engl. 25 (1986) 236.
[31] U. Schubert, New J. Chem. 18 (1994) 1049.
[32] A. Rosenfeld, D. Avnir, J. Blum, J. Chem. Soc., Chem. Commun. (1993) 583.
[33] D. Avnir, Acc. Chem. Res. 28 (1995) 328.
[34] E. Fache, C. Mercier, N. Pagnier, B. Despeyroux, P. Panster, J. Mol. Catal. 79 (1993) 117.
[35] K.J. Balkus, Jr, S. Kowalak, K.T. Ly, D.C. Hargis, Stud. Surf. Sci. Catal. 69 (1991) 93.
[36] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[37] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[38] P.T. Tanev, T.J. Pinnavaia, Science 267 (1995) 865.
[39] D. Brunel, A. Cauvel, F. Fajula, F. di Renzo, Stud. Surf. Sci. Catal. 97 (1995) 173.
[40] C.J. Liu, S.G. Li, W.Q. Pang, C.M. Che, Chem. Commun. (1997) 65.
[41] E.G. Kuntz, Chem. Tech 17 (1987) 570.
[42] P. Kalck, F. Monteil, Adv. Organometal Chem. 32 (1992) 219.
[43] W.A. Herrmann, C.W. Kohlpaintner, Angew. Chem. Int. Ed. Engl. 32 (1993) 1524.
[44] F. Joo, A. Katho, J. Mol. Catal. A: Chem. 116 (1997) 3.
[45] B. Cornils, E.G. Kuntz, J. Organometal Chem. 502 (1995) 177.
[46] R.Z. Moravec, W.T. Schelling, C.F. Oldershaw, Brit. Patent 511 (1939) 556.
[47] G.J.K. Acres, G.C. Bond, B.J. Cooper, J.A. Dawson, J. Catal. 6 (1966) 139.
[48] P.R. Rony, Chem. Eng. Sci. 23 (1969) 1021.

[49] P.R. Rony, J. Catal. 14 (1969) 142.
[50] J. Hjortkjen, M.S. Scured, P. Simonsen, J. Mol. Catal. 6 (1979) 405.
[51] L.A. Gerritsen, J.M. Herman, J.J.F. Scholten, J. Mol. Catal. 9 (1980) 241.
[52] N.A. de Munck, M.W. Verbruggen, J.E. de Leur, J.J.F. Scholten, J. Mol. Catal. 11 (1981) 331.
[53] T. Uematsu, T. Kawakami, F. Saitho, M. Miura, Hashimoto, J. Mol. Catal. 12 (1981) 11.
[54] J.S. Kim, R. Datta, AIchE J. 37 (1991) 1675.
[55] J.P. Arhancet, M.E. Davis, J.S. Merola, B.E. Hanson, Nature 339 (1989) 454.
[56] I.T. Horvath, Catal. Lett. 6 (1990) 43.
[57] I. Gou, B.E. Hanson, I. Toth, M.E. Davis, J. Organometal Chem. 403 (1991) 221.
[58] I. Gou, B.E. Hanson, I. Toth, M.E. Davis, J. Mol. Catal. 70 (1991) 363.
[59] G. Frémy, E. Monflier, J.F. Carpentier, Y. Castanet, A. Mortreux, Angew. Chem. Int. Ed. Engl. 34 (1995) 147.
[60] G. Frémy, E. Monflier, J.F. Carpentier, Y. Castanet, A. Mortreux, J. Catal. 162 (1996) 339.
[61] K.T. Wan, M.E. Davis, Nature 370 (1994) 449.
[62] K.T. Wan, M.E. Davis, J. Catal. 148 (1994) 1.
[63] K.T. Wan, M.E. Davis, J. Catal. 152 (1995) 25.
[64] P. Schneider, F. Quignard, A. Choplin, D. Sinou, New J. Chem. 20 (1996) 545.
[65] L. Tonks, M.S. Anson, K. Hellgardt, A.R. Mirza, D.F. Thompson, J.M.J. Williams, Tetrahedron Lett. 38 (1997) 4319.
[66] S. dos Santos, Y. Tong, F. Quignard, A. Choplin, D. Sinou, J.P. Dutasta, Organometallics 17 (1998) 78.
[67] E.L. Muetterties, Science 196 (1977) 839.
[68] P. Chini, Gazz. Chim. Ital. 109 (1975) 225.
[69] C. Nédez, A. Théolier, F. Lefebvre, A. Choplin, J.M. Basset, J. Am. Chem. Soc. 115 (1993) 722.
[70] G.M. Zanderighi, C. Dossi, R. Ugo, R. Psaro, A. Theolier, A. Choplin, L. D'Ornelas, J.M. Basset, J. Organometal Chem 296 (1985) 127.
[71] K. Weiss, G. Lössel, Angew. Chem. Int. Ed. Engl. 28 (1989) 62.
[72] R. Buffon, A. Auroux, F. Lefebvre, A. Choplin, J.M. Basset, J. Mol. Catal. 76 (1992) 287.
[73] F. Hughes, J.M. Basset, Y. Ben Taarit, A. Choplin, D. Rojas, J. Am. Chem. Soc. 104 (1982) 7020.
[74] A. Choplin, L. Huang, J.M. Basset, R. Mathieu, U. Siriwardane, S.G. Shore, Organometallics 5 (1986) 1547.
[75] N. Homs, A. Choplin, P. Ramirez de la Piscina, L. Huang, E. Garbowski, R. Sanchez-Delgado, J.M. Basset, Inorg. Chem. 27 (1988) 4030.
[76] E. Guglielminotti, A. Zecchina, J. Mol. Catal. 24 (1984) 331.
[77] H.H. Lamb, B.C. Gates, J. Am. Chem. Soc. 108 (1986) 81.
[78] J.M. Basset, A. Théolier, D. Commereuc, Y. Chauvin, J. Organomet. Chem. 279 (1985) 147.
[79] B. Besson, A. Choplin, L. D'Ornelas, J.M. Basset, J. Chem. Soc. Chem. Commun. (1982) 843.
[80] A. Choplin, B. Besson, L. D'Ornelas, R. Sanchez-Delgado, J.M. Basset, J. Am. Chem. Soc. 110 (1988) 2783.
[81] T.R. Krause, M.E. Davies, J. Lieto, B.C. Gates, J. Catal. 94 (1985) 195.
[82] J.P. Scott, J.R. Budge, A.L. Rheingold, B.C. Gates, J. Am. Chem. Soc. 109 (1987) 7736.
[83] D.W. Sindorf, G.E. Maciel, J. Am. Chem. Soc. 105 (1983) 1487.
[84] G.E. Maciel, D.W. Sindorf, J. Am. Chem. Soc. 102 (1980) 7606.
[85] S. Leonardelli, L. Fachinelli, C. Frétigny, P. Tougne, A.P. Legrand, J. Am. Chem. Soc. 110 (1992) 6412.
[86] H. Knözinger, P. Ratnasamy, Catal. Rev. Sci. Engng 17 (1978) 31.
[87] B.A. Huggins, P.D. Ellis, J. Am. Chem. Soc. 114 (1992) 2098.
[88] H.P. Boehm, H. Knözinger, in: J.R. Anderson, M. Boudart (Eds.), Catalysis and Technology, vol. 4, Springer, Berlin, 1983, p. 39.
[89] H. Knözinger, Adv. Catal. 25 (1976) 184.
[90] P.O. Stockart, P.G. Rouxhet, J. Colloid Interface Sci. 86 (1982) 96.
[91] E. Garrone, F.S. Stone, Proceedings 8th International Congress Catalysis, vol. 3, Verlag Chemie, Berlin, 1984, p. 441.
[92] R.N. Spitz, J.E. Barton, M.A. Barteau, R.H. Staley, A.W. Sleight, J. Phys. Chem. 90 (1986) 4067.

[93] A. Choplin, F. Quignard, Trends Inorg. Chem. 3 (1993) 463.

[94] B. Besson, B. Moraweck, J.M. Basset, R. Psaro, A. Fusi, R. Ugo, J. Chem. Soc., Chem. Comm. (1980) 569.

[95] R. Psaro, R. Ugo, B. Besson, A.K. Smith, J.M. Basset, J. Organomet. Chem. 213 (1981) 215.

[96] S.L. Cook, J. Evans, G.S. McNulty, G. Neville-Greaves, J. Chem. Soc., Dalton Trans. 7 (1986) 7.

[97] M. Deeba, B.J. Streusand, G.L. Schrader, B.C. Gates, J. Catal. 69 (1981) 218.

[98] T.H. Walter, G.R. Frauenhoff, J.R. Shapley, E. Oldfield, Inorg. Chem. 27 (1988) 2561.

[99] S.L. Cook, J. Evans, G.N. Greaves, J. Chem. Soc., Chem. Comm. (1983) 1287.

[100] F.B.M. Duivenvoorden, D.C. Köningsberger, Y.S. Uh, B.C. Gates, J. Am. Chem. Soc. 108 (1986) 6254.

[101] L. D'Ornelas, A. Choplin, J.M. Basset, L.Y. Hsu, S.G. Shore, New J. Chem. 9 (1985) 655.

[102] L.Y. Hsu, S.G. Shore, L. d'Ornelas, A. Choplin, J.M. Basset, Polyhedron 7 (1988) 2399.

[103] L.Y. Hsu, S.G. Shore, L. d'Ornelas, A. Choplin, J.M. Basset, J. Catal. 149 (1994) 159.

[104] D. Roberto, R. Psaro, R. Ugo, Organometallics 12 (1993) 2292.

[105] B.C. Gates, J. Mol. Catal. 86 (1994) 95.

[106] D. Roberto, E. Cariati, R. Ugo, R. Psaro, Inorg. Chem. 35 (1996) 2311.

[107] F.D. Hardcastle, I.E. Wachs, J. Mol. Catal. 46 (1988) 15.

[108] Y. Xu, J. Huang, Z. Lin, X. Guo, J. Mol. Catal. 65 (1991) 275.

[109] M. Sibeijn, R. Spronk, J.A. Van Veen, J.C. Mol, Catal. Lett. 8 (1991) 201.

[110] K.P.J. Williams, K. Harrison, J. Chem. Soc., Faraday Trans. 1 86 (1990) 1603.

[111] R. Spronk, A. Andreini, J.C. Mol, J. Mol. Catal. 65 (1991) 219.

[112] C.P. Casey, T.J. Burkhardt, J. Am. Chem. Soc. 96 (1974) 7808.

[113] J.H. Wengrovius, R.R. Schrock, M.R. Churchill, J.R. Missert, W.J. Youngs, J. Am. Chem. Soc. 102 (1980) 4515.

[114] J. Kress, M. Wesolek, J.A. Osborn, J. Chem. Soc., Chem. Commun. (1982) 514.

[115] L.K. Johnson, S.C. Virgil, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 112 (1990) 5384.

[116] F. Quignard, M. Leconte, J.M. Basset, J. Chem. Soc., Chem. Commun. (1985) 1816.

[117] F.N. Tebbe, G.W. Parshall, G.S. Reddy, J. Am. Chem. Soc. 100 (1978) 3611.

[118] L.R. Gilliom, R.H. Grubbs, J. Am. Chem. Soc. 108 (1986) 733.

[119] J.L. Herisson, Y. Chauvin, Makromol. Chem. 141 (1970) 161.

[120] J.P. Soufflet, D. Commereuc, Y. Chauvin, C.R. Hebd, Séances Acad. Sci., Ser. C 276 (1973) 169.

[121] W. Wagner, Ph.D. Thesis, Technische Universität München, 1990.

[122] R. Buffon, A. Choplin, M. Leconte, J.M. Basset, R. Touroude, W.A. Herrmann, J. Mol. Catal. 72 (1992) L7.

[123] R. Buffon, M. Leconte, A. Choplin, J.M. Basset, J. Chem. Soc., Dalton Trans. (1994) 1723.

[124] R.H. Crabtree, Chem. Rev. 85 (1985) 245.

[125] M. Ephritikine, New J. Chem. 10 (1986) 9.

[126] M.L. Green, D. O'Hare, Pure Appl. Chem. 57 (1985) 1897.

[127] I.P. Rothwell, Polyhedron 4 (1985) 177.

[128] A.E. Shilov, G.B. Shul'pin, Russ. Chem. Rev. 59 (1990) 853.

[129] C. Aitken, J.F. Harrod, E. Samuel, J. Organomet. Chem. 279 (1985) C11.

[130] J.F. Harrod, Y. Mu, E. Samuel, Polyhedron 10 (1991) 1239.

[131] T. Don Tilley, Comments Inorg. Chem. 10 (1990) 37.

[132] D.G.H. Ballard, Adv. Catal. 23 (1973) 263.

[133] V.A. Zakharov, V.K. Dudchenko, E.A. Paukhis, L.G. Karachiev, Yu.I. Yermakov, J. Mol. Catal. 2 (1977) 421.

[134] J. Schwartz, M.D. Ward, J. Mol. Catal. 8 (1980) 465.

[135] F. Quignard, A. Choplin, J.M. Basset, J. Chem. Soc., Chem. Commun. (1991) 1589.

[136] F. Quignard, C. Lécuyer, A. Choplin, D. Olivier, J.M. Basset, J. Mol. Catal. 74 (1992) 353.

[137] F. Quignard, C. Lécuyer, A. Choplin, J.M. Basset, J. Chem. Soc., Dalton Trans. 1 (1994) 1153.

[138] C. Lécuyer, F. Quignard, A. Choplin, D. Olivier, J.M. Basset, Angew. Chem. Int. Ed. Engl. 30 (1991) 1660.

[139] B. Coutant, F. Quignard, A. Choplin, J. Chem. Soc., Chem. Commun. (1995) 137.

[140] J.Y. Corey, X.H. Zhu, T.C. Bedart, L.D. Lange, Organometallics 10 (1991) 924.

[141] C.F. de Grauuw, J.A Peters, H. van Bekkum, J. Huskens, Synthesis (1994) 1007.
[142] P. Leyrit, C. McGill, F. Quignard, A. Choplin, J. Mol. Catal. A: Chem. 112 (1996) 395.
[143] K. Inada, M. Shibagaki, Y. Nakanashi, H. Matsushita, Chem. Lett. (1993) 1795.
[144] M. Taramasso, G. Perego, B. Notari, US Patent 4 410 501, 1983.
[145] F. Quignard, A. Choplin, R. Teissier, J. Mol. Catal. A: Chem. 120 (1997) L27.
[146] R.A. Sheldon, J.A. van Doorn, J. Catal. 31 (1973) 427.
[147] W.M. Meier, D.H. Olson, Atlas of Zeolite Structure Types, Butterworth-Heinemann, 1992.