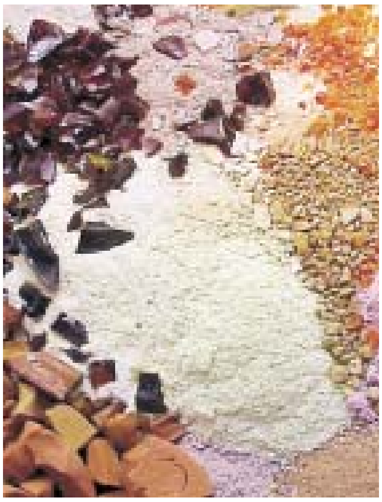
# Making Catalysts by the Sol-Gel Process



by Giovanni Predieri and Daniele Cauzzi

The sol-gel process allows precise control of the synthetic conditions of catalytic materials based on metal or semi-metal oxides. Hydrolytic or non-hydrolytic procedures can be choosen for the production of system with desired properties.
The process also permits the production of inorganic-organic (I.-O.) hybrid systems. Catalytic materials achievable by sol-gel routes are divided in four classes and examples for each class are extracted mainly from the last-three years literature.

The category of catalytic materials comprises those inorganic and hybrid inorganic-organic (I.-O.) solid systems endowed with catalytic activity by virtue of their chemical composition and their structural and textural features. Their preparation requires various synthetic procedures sometimes terminating either in drastic thermal treatments of oxide blends (after impregnation or coprecipitation steps), or in soft immobilization reactions of delicate organometallic species to porous supports [1].

The performance of the final product often appears strongly dependent on rather subtle changes in the process conditions. In this regard, the sol-gel route [2] has intrinsic advantages compared with the other methods, because it allows a precise control of the synthetic conditions and hence of the factors relevant to catalytic activity, such as purity, stoichiometry, homogeneity (or controlled heterogeneity) and microstructural properties of the catalyst or catalyst support. Sol-gel synthesis of catalytic materials was in its infancy about ten years ago and now is a mature, rapid expanding research area; more than five hundred papers have been published in the last three years and a number of authoritative reviews appeared in the last decade [3].

Aim of this paper is to give a survey of the most recent results obtained by applying sol-gel methodologies in the production of inorganic and hybrid I.-O. materials. Far from being exhaustive, this overview first introduces the generality of the sol-gel process, of the hybrid I.-O. materials and of non-hydrolytic sol-gel methods, then it offers representative examples, among the moltitude of catalysts obtained via sol-gel, gathered in classes in dependence on the nature of the active species. The selected examples have been choosen in the most recent literature, with attention to the scientific production of the Italian research groups. By surveying this literature it emerges that working in this field, which lies at the border between molecular chemistry and material science, requires efforts and competences in design, synthesis and characterization both of fine organometallic precursors, and of amorphous, sometimes polycrystalline-multiphasic solids. The full armoury of the solution and solid state spectroscopic, microscopic and scattering tools has often to be deployed to determine both the structure of molecular complexes (precursors or models of anchored active species), and the physicochemical features of porous solids.

## General topics

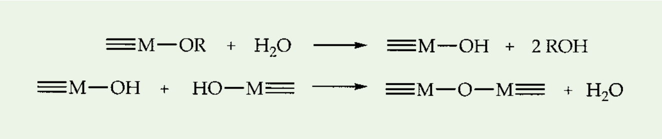
### *The sol-gel process*

The sol-gel process comprises all the synthetic procedures which lead to the formation of amorphous solids starting from solutions of molecular precursors, passing through sol

*$NiMoO_4$ dispersed into silica gel (pale green powder) and the xerogel precursor (green monoliths)*

---

Giovanni Predieri and Daniele Cauzzi, Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica - Università di Parma - Parco Area delle Scienze - 43100 Parma.



*Scheme 1 - Basic hydrolytic sol-gel reactions*

and gel stages, under very soft conditions (generally at room temperature). The chemical processes involved are mostly catalysed hydrolysis and condensation reactions involving metal or semi-metal alkoxides, as depicted in Scheme 1. Metal oxides or oxo-oligomers or polymers are the final results of hydrolysis and condensation reactions. Strict control on homogeneity and textural features of the derived materials (thin films, monoliths, powders) depends on the fine understanding of all the chemical processes involved and then in the choice of the reaction conditions. These include water/alkoxide ratio, nature and concentration of catalysts ($H^+$, $OH^-$ or nucleophiles such as $F^-$), cosolvents, temperature, method and rate of drying, presence of dopants and even chemical nature of the surface of the reaction container. Tipically the final products are highly porous materials with wide pore size distributions and with surface areas usually in the range of several hundreds of squared meters per gram.

Elimination of the solvent from the gel, under ambient conditions, results in a large shrinkage and leads to materials called xerogels. This does not matter for the preparation of dense glassy material, but if one wants to keep the highly porous network of the wet gel, other method of drying have to be employed, such as that with supercritical fluids. It allows the replacement of the pore liquid by air without shrinking of the gel body and the resulting materials are called aerogels [2]. Aerogels in the form of simple or mixed oxides exhibit high surface areas and large pore volumes. Aerogel catalysts show in general greater activities and selectivities than the corresponding xerogels [4].

The composition of the final sol-gel materials may be varied at will either by using mixtures of different hydrolysable alkoxide precursors or by chemical modification of the precursors themselves with organic fragments. The first case leads mainly to the production of oxides and mixed oxides, whereas the second one is particularly suitable for the production of (I.-O.) hybrid materials, where an organic moiety is covalently linked to the central atom in an hydrolysable species. In this regard, most of the current literature on hybrid gels deal with modified silicas [5], but the principles involved are quite general and could be applied to the processing of other main group or transition metal oxides, the limitations being dictated by the strong hydrolysable character of the M-C bonds in transition metals. Scheme 2 reports examples of silane precursors for I.-O. materials.

*Inorganic-organic hybrid materials*

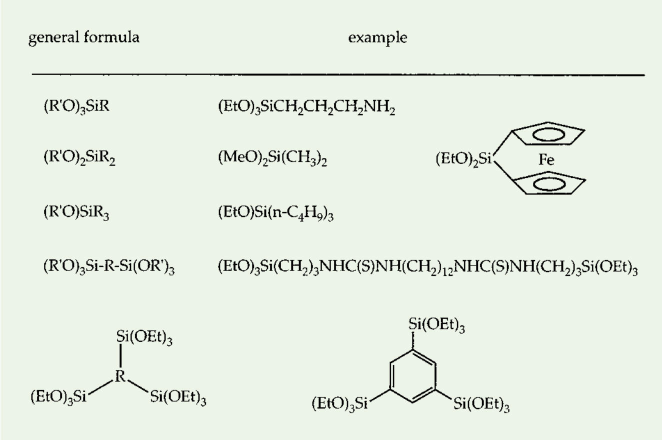
The preparation of a composite from two materials with vastly different physical properties is a recurrent concept in material science, as few pure substances fulfill the demands of modern applications. In this regard, I.-O. hybrid composites and nanocomposites can meet different requirements of modern technology in the fields of adhesive, sealing and modified glass surface materials, sensors, optical devices and artificial membranes [6]. The sol-gel process, originally devoted towards the synthesis of exclusively inorganic polymeric materials, has gained growing interest as an effective method to prepare I.-O. hybrid materials, either by incorporating organic molecules in the oxide networks [7], or by hydrolysis and condensation of organically substituted alkoxysilanes such as $RSi(OR')_3$ [5], as stated at the end of the previous section.

The mild synthetic conditions offered by the sol-gel process allow the design of these hybrids materials where inorganic and organic components can be mixed at the nanometric scale in virtually any ratio, leading to the so-called I.-O. nanocomposites [8]. Considering the case of organically substituted alkoxides, it is possible to obtain hybrid materials whose physico-chemical properties depend on the nature of the R group. Recent work has also pointed out the potential of I.-O. hybrids for the controlled preparations of purely inorganic amorphous materials with tuned porosity after elimination of the organic component [9].

*Non-hydrolytic procedures*

Most sol-gel preparation procedures are aqueous, but a very interesting chemistry is being developed [10] in order to overcome certain disadvantages due to water presence. In fact, when sol-gel method is used for highly reactive transition metal alkoxides, it is sometimes difficult to control the process: precipitation instead of gelation is often observed. Moreover, when uniform binary oxides are desired, the rate of hydrolysis and condensation of the individual precursors must be comparable in order to avoid segregation of one of the oxides.

Consequently, when transition metal alkoxides are processed with less reactive derivatives, such as silicon alkoxides, the latter are partially hydrolyzed prior to mixing. Alternately or simultaneously a complexing agent is introduced (carboxylic acids or β-diketonates [11]) to reduce the hydrolysis rate of the transition metal species. By this way co-hydrolysis and co-condensation can be achieved affording xerogels which can contain unsymmetrical M-O-M' linkages. Subsequent thermal treatment of these materials yields, in some cases, crystalline mixed-oxide phases, without segregation. One route to evade this complication is the so called non-hydrolytic sol-gel process, M-O-M' bonds being obtained by direct reaction between suitable oxygen containing precursors. In general, these reactions are called aprotic condensations, water being not required for



*Scheme 2 - Silane precursors for I.-O. materials* hydrolysis, nor produced by condensation [12]. A general scheme of non-hydrolytic processes is depicted in Scheme 3. The most convenient path is the reaction of metal chlorides with metal alkoxides, alkyl chlorides being obtained as side products and easily separated from the solid. Normally the reaction is carried out without solvents in closed vessels to avoid loss of volatile precursors (i.e. $SiCl_4$), but sometimes the desired product can form by simple heating under reflux below the boiling points of the reactants owing to the high reactivity of the precursors.

The rough material obtained by this method normally contain residual chloride and alkoxy groups, which are further removed by thermal treatment, obtaining a single oxide or a mixture of phases, depending on the kinetic and thermodynamic properties of the system. When the presence of chloride ions is not desired, condensation of alkoxides with metal esthers can be used.

The main advantages intrinsic in this methods, compared the hydrolytic route, are:

(i) low temperature to unhydrated and low-hydroxyl oxides;
(ii) improved control over the molecular level homogeneity and stoichiometry of multicomponent oxides;
(iii) possible access to new structures, otherwise broken by hydrolysis;
(iv) easily removable by-products.

In this way, silica, alumina and transition metal oxides gels, as well as binary oxides in the systems $Al_2O_3$-$SiO_2$, $TiO_2$-$SiO_2$ and $ZrO_2$-$SiO_2$ [13], have been prepared. More recently crystalline $ZrTiO_4$ has been obtained from a non-hydrolytic gel of the same composition [14].

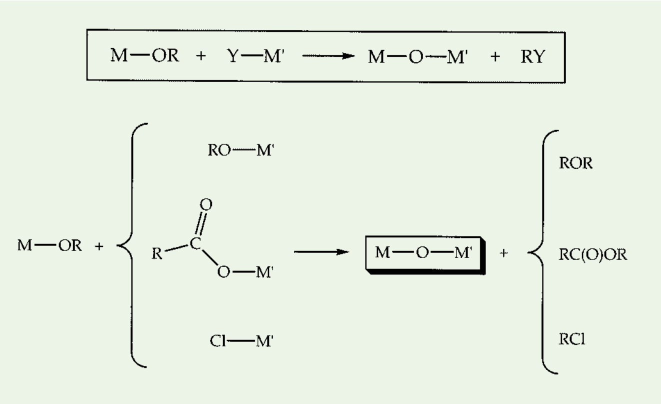
## Classes of catalysts obtained via sol-gel

### *Uniphasic or multiphasic oxides or mixed oxides*

This class encompasses a variety of materials whose common characteristic is the presence of M-O-M or M-O-M' linkages. The uniphasic systems span from simple stoichiometric oxides or mixed oxides to atomic dispersion of metal cations in oxide matrices (as it occurs in amorphous metallosilicates). The multiphasic ones comprise dispersions of single or mixed oxide phases in oxides matrices.

Practically all important metal or semimetal oxides have been prepared by the sol-gel process [2] and there is now an upsurging interest in the sol-gel synthesis of mixed oxides, such as alumina-silica, alumina-titania, titania-silica and zirconia-silica [15]. In this context, the mechanisms responsible for phase separation in gel-based synthesis of multicomponent metal oxides have been surveyed [16]. Moreover, a recent review report the results on characterization and applications of titania-silica materials (mostly prepared via sol-gel) as photocatalysts, acid catalysts and oxidation catalysts [17].

In fact, the applications of sol-gel materials in catalysis mostly deals with mixed-oxide or doped single-oxide systems (rather than with pure single oxides) in order to get advantage from synergistic effects. In this regard, sulphate-doped $ZrO_2$ and $ZrO_2$-$Al_2O_3$ catalysts for the isomerization of paraffins have been prepared by Italian researchers via sol-gel procedures [18]. Furthermore, a series of aluminosilicates with similar silica/alumina ratios and similar structural properties of natural pumice was prepared starting from the appropriate alkoxides [19]. Most catalytic applications of sol-gel derived oxide catalysts regard oxidations and in particular olefin oxidations. In this general context, two recent papers deal respectively with silicate xerogels containing cobalt for the side-chain oxidation of alkyl aromatics with *tert*-butyl hydroperoxide [20] and sol-gel Bi-Mo-Ti mixed oxides for the gas-phase oxidation of butadiene to furan [21].



*Scheme 3 - Aprotic condensation processes*

Our investigations in this field has regarded both the aqueous preparation of silica supported bismuth, nickel and copper molybdates [22] and the non-hydrolytic synthesis of $NbVO_5$ [23] starting from $VO(OiPr)_3$ and $NbCl_5$.

This compound, absent in the phase diagram of the $V_2O_5$-$Nb_2O_5$ system, appears to be accessible only by sol-gel procedures. In the case of the system $CuMoO_4/SiO_2$, EPR investigations [22c] have demonstrated that the sol-gel method is superior to impregnation in producing homogeneous dispersion of the active phase.

Regarding $NiMoO_4/SiO_2$, the sol-gel synthesis lead to the formation of $NiMoO_4$ crystallites encapsulated in the silica matrix, in such a way that the unstable β-phase is 'stabilized' at room temperature [22b].

### *Dispersions of metal colloids in oxide matrices*

Nanocomposite materials consisting of colloidal metal particles (diameter less then 100 nm) dispersed throughout a host matrix are of interest for potential applications in catalysis or as magnetic, electronic or photonic materials.

This kind of catalysts prepared via sol-gel processing generally consist of very small metal particles which are homogeneously distributed inside the support.

The key to control the particle size is the high dispersion of the metal precursor during the sol-gel step. The encapsulation of the metal colloids into oxide matrices results in a greater thermal stability against sintering compared to catalysts prepared with conventional methods.

Most of the dispersed-metal catalysts prepared by sol-gel derive from the reduction of metal salts or complexes (anchored or not) dispersed in xerogel matrices. Both mono- and bimetallic systems have been obtained by this route.

Recent achievements include the production of crystalline nanoclusters of Ag, Cu, Os, Pd, Pt, Re, or Ru in a silica xerogel matrix [24], of silica supported Pd-Co bimetallic catalysts for CO hydrogenation [25], of low density xerogel Pd-Ag/$SiO_2$ catalysts for hydrodechlorination of 1,2-dichloroethane [26] and of Ag/$Al_2O_3$ and Ag-Au/$Al_2O_3$ composite systems for the reduction of $NO_x$ by propene [27]. A promising variation to the above reported methods consists in the use of metal carbonyl clusters as precursors for metal colloids. This procedure combines the main advantages of using molecular clusters (low activation temperature, size control, high dispersion, absence of undesired anions) with those of the sol-gel process (homogeneity, texture and porosity control).

The use of $Ru_3(CO)_{12}$ to prepare $Ru/SiO_2$ catalysts, for the Fischer-Tropsch reaction, afforded higher metal dispersions and catalytic activities than $RuCl_3$ [28]. Similarly, mixed metal clusters could be employed to prepare dispersed mixed metal colloids.

*Molecular species covalently bound to oxides matrices*

Catalysts with active molecular species linked to a siloxane matrix are easily obtained by the co-polymerization of a silica precursor, such as $Si(OEt)_4$, with a trialkoxy(organo) silane $RSi(OR')_3$, as previously mentioned. When R contains an electron donor function L, the material is able to bind different metal species by coordinative interactions, affording systems which are potential heterogenized homogeneous (hybrid) catalysts.

Furthermore, the co-hydrolysis and condensation of the substituted alkoxide $(RO)_3Si(CH_2)_n$-L with increasing amounts of $Si(OR)_4$ produce polymeric materials with decreasing density of ligating functions, offering the possibility to study the catalytic activity of a particular metal complex as a function of the abundance of the donor groups.

Generally this synthetic procedure provides robust materials with a higher and controlled content of available ligand group than their silica immobilized counterparts produced by reaction of a functionalized alkoxysilane with the surface silanol groups [29]. The physico-chemical characteristics of these xerogels, such as the robustness, the high surface area, the availability of a suitable ligand group, make them very attractive supporting materials for heterogeneous and hybrid metal catalysis.

The phosphine and amine groups tethered to silica are the most common binding functions, but oxygen and sulfur ligands have been used as well. Indeed, depending on the nature of the metal species and on the metal anchoring conditions, both tethered metal complexes [30] and supported small metal particles with catalytic activity [31] have been prepared starting from hybrid sol-gel materials.

The chemical reactions occurring on an anchored metal center inside I.-O. hybrid materials are better understood by applying the concept of interphase, which was firstly introduced in reversed phase chromatography [32].

Interphases are defined as particular regions within a material in which a solid and a liquid component penetrate each other on a molecular level. In these regions, a reactive center becomes highly mobile, thus simulating the properties of a solution. Thus catalysts are available which provide favourable activities in the hydrogenation and hydroformylation of unsaturated substrates and the copolymerization of alkenes with carbon monoxide, without any marked leaching of the active transition metal catalysts [33].

Recently, the accessibility of phosphorus centres incorporated into I.-O. hybrid xerogels has been investigated [34] and it has been found that the availability to form metal complexes depends on the structure of the precursors, the degree of condensation of the polysilsesquioxane $RSiO_{3/2}$ network and the specific surface area of the material. Similar results have been obtained by us with thiourea-functionalized xerogels, where the accessibility of ligand functions by rhodium(I) is strongly dependent on the age of the gel, the young ones exhibiting the maximum accessibility [35].

*Molecular species entrapped in oxide matrices*

Entrapment in oxide xerogels, can be easily achived by adding the molecular species to the polymerizing mixture at an early stage and when the polycondensation is completed the dopant molecules are incapsulated in the inorganic network. Both metal complexes and organic molecules with catalytic activity can be subjected in principle to this treatment. Unlike the catalysts described in the previous section, in these hybrid systems the active species are not covalently linked to the oxide matrices. It has been pointed out that covalent binding approach requires multistep chemical modifications, which can be circumvented by using the direct physical entrapment method, which has been recently reviewed [36].

The caging is often associated with improving in the stability of the active species and in its catalytic activity and makes it possible to recover and recycle the catalytic material. Very recently, stable nitroxyl radicals have been entrapped in silica xerogels leading to efficient catalysts for the selective oxidation of *D*-methylglucose and cynnamyl alcohol either in water or in organic solvents, without appreciable leaching [37].

## Concluding remarks

This survey should have shown that sol-gel methods have a broad field of applications in catalysis leading to the production of a wide variety of catalytic materials. It must be remarked, however, that an important related area not surveyed in this paper is that of biocatalytic materials deriving from entrapment or immobilization of enzymes, cells or microorganisms in silica xerogel matrices [38].

The many possibilities of chemically modifying the precursor systems and of choosing the experimental conditions, together with the other inherent advantages of the sol-gel process, allow the deliberate tailoring of material properties over a wide range. In fact, by these methods it is possible to create M-O-M' linkages, to encage and protect delicate molecular catalysts, to obtain fine dispersion of metal colloids in host oxide matrices, and to produce I.-O. hybrid materials with desired active functions. It has been shown that supported reagent type catalysts can be easily obtained from these I.-O. materials.

They have proved their value in many organic reactions as environmentally friendly replacements for established reagents responsible for unacceptable chemical waste. In this regard, metal leaching is still a serious drawback for surface modified materials [39], however, it is confidently expected that strong covalent bindings and optimized cross-linkages in the I.-O. polymers would at last impede metal leaching. Although sol-gel process is intrinsically unable to generate ordered arrays, it is possible to create ordered arrangements of pores, with a narrow distribution of pore sizes, by employing micellar arrays of surfactants molecules as structure directing agents. Very recently, the synthesis of highly ordered macroporous structures of inorganic oxides, phosphates and hybrid composites has been accomplished from metal alkoxides precursors templated around polystyrene microspheres [40]. These were ordered into close-packed arrays by centrifugation. Finally, the feasibilty to achieve chiral I.-O. hybrid solids for molecular recognition and asymmetric catalysis by sol-gel techniques has been lately explored. As an example, new enentioselective catalytic materials have been obtained by sol-gel processing alkoxysilyl-substituted chiral diammine-rhodium complexes [41]. ◆

## References

[1] G. Ertl, H. Knözinger, J. Weitkamp, Handbook of Heterogeneous Catalysis, Vol. 1, VCH, Weinheim, 1997; B. Cornils, W.A. Hermann, Applied Homogeneous Catalysis with Organometallic Compounds, Vol. 2, VCH, Weinheim, 1996; J.A. Schwarz, C. Contescu, A. Contescu, *Chem. Rev.*, 1995, **95**, 477; T.J. Barton, L.M. Bull *et al., Chem. Mater.*, 1999, **11**, 2633.

[2] C.J. Brinker, G.W. Scherer, Sol-Gel Science, Academic Press, S. Diego, 1990; L.L. Hench, J.K. West, *Chem. Rev.*, 1990, **90,** 33.

[3] M.A. Cauqui, J.M. Rodriguez-Izquierdo, *J. Non-Cryst. Solids,* 1992, **147,** 148; U. Schubert, *New J. Chem.*, 1994, **18,** 1049; R.D. Gonzales, T. Lopez, R. Gomez, *Catal. Today,* 1997, **35,** 293; J.B. Miller, E.I. Ko, *Catal. Today,* 1997, **35,** 269.

[4] G.M. Pajonk, *Appl. Catal.*, 1991, **72,** 217.

[5] D.A. Loy, K.J. Shea, *Chem. Rev.,* 1995, **95,** 1431 and references therein.

[6] S. Dirè, F. Babonneau *et al., J. Mater. Chem.,* 1997, **7,** 67.

[7] D. Avnir, *Acc. Chem. Res.,* 1995, **28,** 328.

[8] C. Sanchez, F. Ribot, B. Lebeau, *J. Mater. Chem.,* 1999, **9,** 35.

[9] P. Chevalier, R.J.P. Corriu *et al., New. J. Chem.,* 1998, 423.

[10] R.J.P. Corriu, D. Leclercq *et al., Chem. Mater.,* 1992, **4,** 961.

[11] C. Sanchez, J. Livage *et al.*, *J. Non-Cryst. Solids,* 1988, **100,** 65.

[12] A. Vioux, *Chem. Mater.,* 1997, **9,** 2292.

[13] M. Andrianainarivelo, R.J.P. Corriu *et al., J. Mater. Chem.,* 1996, **6,** 1665.

[14] M. Andrianainarivelo, R.J.P. Corriu *et al., J. Mater. Chem.,* 1997, **7,** 279.

[15] J.M. Miller, L.J. Lakshmi, *J. Phys. Chem. B,* 1998, **102,** 6465 and references therein.

[16] Y. Narendar, G.L. Messing, *Catal. Today,* 1997, **35,** 247.

[17] X. Gao, I.E. Wachs, *Catal. Today,* 1999, **51,** 233.

[18] G. Strukul, M. Signoretto *et al.,* Atti del Workshop Italiano Sol-Gel, Padova, 1999, Cusl (PD), 74.

[19] L.F. Liotta, A.M. Venezia *et al, J. Catal.,* 1997, **171,** 169.

[20] M. Rogovin, R. Neumann, *J. Mol. Catal. A,* 1999, **138,** 315.

[21] M.D. Wildberger, T. Mallat *et al., Appl. Catal. A,* 1999, **179,** 189.

[22] a) D. Cauzzi, G. Predieri *et al.,* in B. Delmon *et al.* (Eds.), Preparation of Catalysts VII, Elsevier, Amsterdam (NL), 1998, 699; b) D. Cauzzi, G. Predieri *et al., Appl. Catal. A,* 1999, **182,** 125; c) F. Morazzoni, G. Predieri *et al., J. Mater. Chem.,* 1999, **9,** 507.

[23] D. Cauzzi, G. Predieri *et al.,* Proceedings of 6th European Workshop on Selective Oxidation, Rimini (I), 1999, SCI Publ., Rome, 57.

[24] J.P. Carpenter, C.M. Lukehart *et al., Chem. Mater.,* 1997, **9,** 3164.

[25] L. Guczi, Z. Schay *et al., J. Mol. Catal. A,* 1999, **141,** 177.

[26] B. Heinrichs, P. Delhez *et al., J. Catal.,* 1997, **172,** 322.

[27] E. Seker, J. Cavataio *et al., Appl. catal. A,* 1999, **183,** 121.

[28] P. Moggi, G. Predieri, F. Di Silvestri *et al., Appl. Catal.,* 1999, **182,** 257.

[29] I.S. Khatib, R.V. Parish, *J. Organomet. Chem.,* 1989, **369,** 9.

[30] U. Schubert, C. Egger *et al., J. Mol. Catal.,* 1989, **55,** 330; D. Cauzzi, G. Predieri *et al., J. Organomet. Chem.,* 1997, **541,** 377; H. Schumann, D. Avnir *et al., Inorg. Chim. Acta,* 1998, **280,** 21; E. Lindner, A. Jäger *et al., Chem. Mater.,* 1998, **10,** 217; O. Kröcher, R.A. Köppel, A. Baiker, *J. Mol. Catal. A,* 1999, **140,** 185.

[31] J.M. Tour, S.L. Pendalwar, J.P. Cooper, *Chem. Mater.,* 1990, **55,** 3452; P. Hernan, C. del Pino, E. Ruiz-Hitzky, *Chem. Mater.,* 1992, **4,** 49; W. Mörke, R. Lamber, U. Schubert, *Chem. Mater.,* 1994, **6,** 1659; D. Cauzzi, G. Predieri *et al., J. Mater. Chem.,* 1995, **5,** 1375.

[32] J.G. Dorsey, K.A. Dill, *Chem. Rev.,* 1989, **89,** 331.

[33] E. Lindner, T. Schneller *et al., Angew. Chem. Int. Ed.,* 1999, **38,** 2154 and references therein.

[34] J.P. Bezombes, C. Chuit *et al., J. Mater. Chem.,* 1999, **9,** 1727.

[35] D. Cauzzi, G. Predieri *et al., J. Organomet. Chem.,* 2000, **593-594,** 431.

[36] J. Blum, D. Avnir, H. Schumann, *Chemtech,* 1999, Febr., 32, and references therein.

[37] R. Ciriminna, M. Pagliaro, D. Avnir, Atti del Workshop Italiano Sol-Gel, Padova, 1999, Cusl (PD), 65.

[38] G. Carturan, R. Dal Monte *et al., J. Sol-Gel Sci. Techn.,* 1998, **13,** 273.

[39] R. Sheldon, M. Wallau *et al., Acc. Chem. Res.,* 1998, **31,** 485.

[40] B.T. Holland, C.F. Blanford *et al., Chem Mater.,* 1999, **11,** 795.

[41] A. Adima, J.J.E. Moreau *et al., J. Mater. Chem.,* 1997, **7,** 2331.

**Acknowledgments:** Financial support from Murst (COFIN 98, “Metal clusters, basic and functional aspects”) is gratefully acknowledged.

### Materiali per la catalisi del processo sol-gel

Il processo sol-gel permette un accurato controllo sulle condizioni di sintesi di materiali per la catalisi basati su ossidi di metalli o semimetalli e quindi sui fattori che determinano la loro attività catalitica come la purezza, la composizione, l’omogeneità e le proprietà strutturali. Sia le tecniche sol-gel idrolitiche, sia quelle non idrolitiche sono a disposizione per la sintesi di sistemi con le proprietà desiderate. Inoltre le blande condizioni di reazione tipiche del processo sol-gel permettono la produzione di materiali ibridi inorganici-organici (I.-O.) sia mediante intrappolamento di molecole organiche nello scheletro polimerico, sia per trattamento idrolitico di precursori alcossidici sostituiti con gruppi organici. I materiali catalitici ottenibili via sol-gel vengono raggruppati in quattro classi delle quali vengono presentati esempi significativi tratti soprattutto dalla letteratura degli ultimi tre anni.