Journal of Non-Crystalline Solids 147&148 (1992) 724–738
North-Holland

JOURNAL OF
NON-CRYSTALLINE SOLIDS

Section 15. Catalysts

Application of the sol–gel methods to catalyst preparation

M.A. Cauqui and J.M. Rodríguez-Izquierdo

Departamento de Química Inorgánica, Universidad de Cádiz, Apartado 40, Puerto Real 11510, Spain

Sol–gel methods have been recognized as interesting procedures to prepare catalysts. The versatility of the sol–gel techniques allows control of the texture, composition, homogeneity and structural properties of solids, and makes possible production of tailored materials such as dispersed metals, oxidic catalysts and chemically modified supports. In this work, different approaches, described in the literature, to prepare catalysts by the sol–gel methods, including both aerogel and xerogel active solids, are reviewed. In parallel, some of the most relevant catalytic reactions carried out with sol–gel catalysts are evaluated.

1. Introduction

The design and characterization of solid catalysts is now recognized as an area of major interest in chemistry and chemical engeneering. More than 90% of the processes carried out by the chemical industries take advantage of the use of catalysts [1]. In the case of the industrialized countries, the use of catalysts is, in some way, involved in the generation of about 20% of the gross national product. In a recent article about the growth of the chemical industry in the USA, the key role of several catalysts as promoters of the economic development of the country was shown [2]. The implantation of new technologies for energy conversion or for the protection of the environment are also in close connection with the use of catalysts [1].

The significance of catalysis is often overlooked, probably because its importance lies in the magnitude of the products or the interest of the processes which require their use, rather than in the value of the catalysts themselves. Catalyst preparation usually involves complex processes, not always understood in detail, the performance of the final product being very sensitive to rather subtle changes in the synthesis procedures. The sol–gel route, because of the possibility of controlling many of the variables involved in solid synthesis, can be considered as an extremely interesting way of preparing materials to be used as catalysts.

In the proceedings of previous International Workshops on Glasses and Ceramics from Gels we found only two papers [3,4] dealing with catalyst preparation and use. This has increased in the 1991 edition to eight papers, in better agreement with the significance of the sol–gel methods in catalysis.

In ref. [5] we can find a rough classification of different types of solids as a function of their catalytic abilities. According to this first approach, we distinguish metals, semiconducting oxides, insulator oxides and solid acids. These catalytic materials can be prepared as bulk solids or, more often, as nanometer-sized particles dispersed on a matrix, thus leading to composite materials usually exhibiting improved catalytic performances. As will be shown in this paper, it is possible to find literature examples of the preparation of all of the above-mentioned types of catalysts through the sol–gel methods. In many cases, sol–gel catalysts show rather unique catalytic properties.

The goal of catalytic processes is to obtain high levels of catalytic activities or high values of reaction rates. Since the conversion of reagents into products takes place over definite sites on the surface of the solid, which are known as active sites, the higher the number of sites, and

0022-3093/92/$05.00

the higher the specific activity per site, the higher activity will be exhibited by the solid. This points to the interest of increasing the number of sites and controlling their nature during the catalyst preparation steps in order to obtain high activity. It is also important to take care of the accessibility of the reactants to the active sites under reaction conditions. For the case of catalytic processes which can take place throughout several parallel or consecutive reactions, it is desirable to obtain high yields of definite products. In this case, a second goal would be to use a catalyst showing good selectivity towards the desired reaction products. This property would be also related to the nature of the active sites, the knowledge of the reaction kinetics, and the control of the operating conditions.

The number and properties of the active sites and the reaction kinetics depend on several factors which can be controlled to some extend by the sol–gel methods of solid synthesis. These factors include: (a) high specific surfaces; (b) controlled pore size distribution; (c) textural stability under the preparation and reaction conditions; for supported catalysts; (d) the active phase must be at the surface, and not homogeneously distributed into the solid, and (e) must present a good and homogeneous dispersion; (f) structural properties must be controlled in order to get the desired crystalline variety or an amorphous structure if preferred; (g) purity of the catalyst components would be as high as possible (contaminants use to concentrate at the surface of solids and small content of impurities on a weight basis can lead to high surface impurities concentration); (h) easily controlled composition, especially for the preparation of multicomponent catalysts, or catalysts promoted by small concentrations of an additive; (i) mechanical properties must accomplish the requirements of the operation conditions; and (j) the catalysts should be active for as long as possible without severe deactivation due to chemical or physical blocking of active sites.

In this article, we discuss examples from the literature of some applications of the sol–gel and related techniques to the preparation of support materials, for the modification of solid surfaces in order to obtained catalytically active solids, and in the preparation of catalysts in a generic way, thus illustrating the contribution of the sol–gel methods to the above-mentioned aspects.

The scope of the work is broad, including materials prepared from alkoxides in organic media, and from inorganic precursors in aqueous solutions. For this reason, a full coverage of all the literature on the subject is not possible within the extent of this paper.

The number of research groups working systematically on sol–gel methods applied to catalyst preparation is very small, although it is easy to find papers in which some of the varieties of the sol–gel procedures are used in order to synthesize catalytic materials. There is no doubt that the group working at the Claude Bernard University in Lyon has made the most extensive research in this field, with more than 70 published papers on the application of aerogel materials in catalysis. For this reason, we will comment first on the more coherent work on aerogels, and later the more dispersed applications based on the use of other methods.

2. Applications of aerogels in catalysis

Many of the significant aspects, pointed out in the Introduction affecting number and properties of the active sites, can be controlled if the aerogel route is used to synthesize a catalyst or a catalytic support material. In fact, general properties of aerogels include well developed textural properties, high purity, possibility of preparing multicomponent systems with broad ranges of compositions, and high homogeneity and good dispersion of minor components. Several general articles are focussed on [6,7] or make reference to [8–10] the use of aerogels in catalysis. A recent, comprehensive review by Pajonk [7] deserves special mention, covering the preparation, characterization, reactivity and some of the problems associated to the design of reactors to be operated with such a type of solid.

2.1. Claude Bernard University work

In 1968 Nicolaon and Teichner [11] proposed a new method for the preparation of silica aerogels starting from alkoxides in alcoholic solution. This method was extended to the preparation of other single- and multicomponent inorganic oxides [8]. It is significant that this new way of preparing aerogels, which remains the most extensively used at present, was proposed by a research group working on heterogeneous catalysis. The method allowed fast processing of the reactants (a few hours), compared with the technique proposed by Kistler [12] (several weeks). This new method can be considered as one of the most important advances in sol–gel science.

Table 1 presents a general overview of different types of aerogel materials, developed by Teichner, Pajonk and co-workers, and their catalytic applications. We focus our discussion on several groups of reactions – hydrogenations (and spillover effect), selective oxidations and nitroxidations – which have been considered in detail by these authors.

2.1.1. Hydrogenation reactions on aerogel catalysts

This reaction type is characteristic of metal catalysts. Cu–Al_2O_3, Cu–SiO_2 and Cu–MgO aerogels have been used for the selective hydrogenations of cyclopentadiene into cyclopentene and of acetylene into ethylene [13–17]. Some of these papers deal with engineering problems in order to carry out the first reaction under integral [16] or fluidized [17] conditions. The selectivities were in all cases very high, with less than 5% of conversion into total hydrogenation products.

The hydrogenation of benzene has been studied on Ni–MoO_2 [18,19] and Pt–MoO_2 [20] catalysts. MoO_2 prepared as aerogel can strongly interact with Ni and Pt under reducing conditions, leading to the enhancement of the specific activities of the metals. The phenomenon seems to be related to formation of some type of new active site associated with intermetallic compounds, such as the $MoNi_4$, and with the existence of electronic interactions between the metal and the support. Ni–SiO_2 [21] has been used as catalyst for a similar reaction (toluene → methylcyclohexane) which can be of potential interest for hydrogen storage. This catalyst can be efficient for the conversion of toluene under integral operation conditions.

In most of the works cited above, the support material was prepared as an aerogel and the metal deposited on the surface by impregnation with solutions of metal salts. In these cases, the metal must be activated by reduction in hydrogen before the catalytic reaction. Alternatively, the metal precursor can be introduced in the gelling solution to avoid the impregnation step. If deal-

Table 1
Aerogel catalytic materials (from ref. [7])

Single oxide		Binary oxides		Ternary oxides (NO, PO) [a]		Metal-oxide (H) [a]
SiO_2	S, SP [b]	NiO-Al_2O_3	PO, NO	NiO-SiO_2-Al_2O_3		Pt-SiO_2
Al_2O_3	S, SP	NiO-SiO_2	NO	NiO-Al_2O_3-MgO		Ni-SiO_2
ZrO_2	S, SP, P	NiO-MgO	NO, AS	NiO-SiO_2-MgO		Ni-Al_2O_3
TiO_2	S, PH	V_2O_5-MgO	AS	NiO-Fe_2O_3-Al_2O_3		Ni-SiO_2-Al_2O_3
ThO_2	PO	Cr_2O_3-Al_2O_3	NO	NiO-V_2O_5-MgO	AS	Ni-SiO_2-MgO
Cr_2O_3	PO	PbO-Al_2O_3	NO	NiO-MgO-Al_2O_3		Cu-Al_2O_3
Fe_2O_3	PO	PbO-ZrO_2	NO	Fe_2O_3-NiO-Al_2O_3		Cu-SiO_2
MoO_2	S	Fe_2O_3-Al_2O_3	FT	Cr_2O_3-Al_2O_3-MgO	NA	Cu-MgO
NiO		Fe_2O_3-SiO_2	FT	Cr_2O_3-Fe_2O_3-MgO	NA	Ni-MoO_2
CuO		CuO-Al_2O_3	PO	Cr_2O_3-Fe_2O_3-Al_2O_3	NA	Pt-MoO_2
PbO						Pd-Al_2O_3
V_2O_5						Cu-ZrO_3
						Cu-ZrO_2-Al_2O_3
						Cu-ZnO-Al_2O_3

[a] In parentheses: applications developed for all the series of catalysts.

[b] S, support; SP, spillover; H, hydrogenation; PO, partial oxidation; NO, nitroxidation; PH, photocatalysis; AS, ammonia synthesis; NA, (NO + NH_3); FT, Fisher–Tropsch.

ing with metals which are easy to reduce, the reduction process can take place in the autoclave during the hypercritical drying of the metal–support gel. It is thus possible to obtain a supported metal catalyst in a single step. That is the case for the Ni–Al_2O_3 aerogels [6,22]. It has been proved that filling the autoclave with hydrogen can contribute to higher levels of metal reduction. Ni–Al_2O_3 catalysts prepared in this way have been used in the hydrogenolysis of ethylbenzene giving benzene, toluene and methane as reaction products.

A phenomenon of great relevance in catalysis is the spill-over effect [23,24]. Hydrogen can be activated and migrate from dispersed metal particles to the support. Teichner and co-workers, using aerogel materials, established that migration of hydrogen can take place by mechanical contact between a dispersed metal catalyst and an oxide material [22], and that this effect can generate new active sites on the oxide surface with catalytic properties which are attributed to metal catalysts [25–29]. Silica or alumina aerogels can be activated by hydrogen spillover presenting catalytic properties in the hydrogenation and hydrogenolysis of hydrocarbons [25–29]. The high specific surface of aerogels, the degree of surface hydroxylation and the heterogeneity of their surfaces can contribute to enhance the spillover effect.

2.1.2. *Selective oxidation reactions*

Single or mixed oxides which include transition-metal cations present catalytic properties for oxidation reactions. Partial oxidations, when carried out with high selectivities, lead to the formation of products of particularly high added value. Teichner and co-workers have studied selective oxidation of alkenes and alkanes on NiO–Al_2O_3 [30–32], NiO–SiO_2–Al_2O_3 [31] and CuO–Al_2O_3 aerogels [33].

Isobutene can be converted into methylacroleine and acetone on NiO–Al_2O_3 catalysts with 67% and 25% selectivities, respectively [30]. In the catalysis literature, oxidation of parafins has been more scarcely studied because of the difficulties of avoiding the total oxidation to CO_2. Isobutane and propane are transformed into acetone with near 100% selectivities on NiO–Al_2O_3 and NiO–SiO_2–Al_2O_3 [30–32], at low temperatures (< 300°C). These selectivities can be achieved when the catalysts are hydroxylated by pretreatment with water vapour at 300°C. This pretreatment inhibits the activity of the stronger sites which are responsible for the total oxidation reactions.

Another example of oxidation of isobutane into acetone was reported in ref. [34]. A TiO_2 aerogel is compared with other titania samples as a photocatalyst for such reaction at ambient temperature.

2.1.3. *Nitroxidation reactions*

Ammoxidation of alkenes (reaction with $NH_3 + O_2$) is the conventional way of obtaining nitriles. This type of compound, and acrylonitrile in particular, is the starting reagent for the production of acrylic fibers and nylon 66. A alternative process for the production of nitriles from a mixture of hydrocarbons and NO, using aerogel catalysts, was proposed by Zidan et al. [35,36] and developed at Lyon. A review on the use of gel catalysts for this reaction has recently appeared [37].

NiO–Al_2O_3 [37–48] and other aerogel materials of related composition are very efficient catalysts for this reaction leading to selectivities into nitriles higher than 90%. The starting hydrocarbon can be an alkene, such as propylene [38–40, 48] or isobutene [40,41], an aromatic compound such as toluene [47], or even an alkane, such as isobutane [41,42]. In the last case, dehydrogenation to alkane takes place before nitroxidation [41]. This can be an interesting method of valorization of alkanes. Selectivity and stability of the catalysts with time on stream can be modulated by the selection of the support [43–45], SiO_2–Al_2O_3, SiO_2, MgO–Al_2O_3, and through the addition of some other minor components such as MgO [40,43,44,48,49] or Fe_2O_3 [41,42,48,49]. The active centers for the reaction seem to be surface Ni^{2+} cations in the form of a $NiAl_2O_4$ spinel-like compound [38,43–47]. The acidity of the support, Al_2O_3 or SiO_2–Al_2O_3, can produce cracking, leading to lower nitriles (acetonitrile from propene), thus decreasing the selectivity in the main nitrile. The addition of a component with basic properties, MgO [48], can decrease the acidity and avoid this problem. The inclusion of Fe_2O_3 improves the stability of the catalyst allowing the conversion of CO into CO_2 by means of the water gas shift reaction [49]. Fe_2O_3 is also interesting as promoter for dehydrogenation, the first reaction step for the nitroxidation of alkanes [41].

More recently, PbO/Al_2O_3 catalysts [50] have been used for the synthesis of dinitriles starting from ortho, meta or para tolunitriles.

2.2. Other works on aerogels

As mentioned above, the number of papers from other labs on this subject is limited. We comment first on some of those works dealing with fundamental catalytic studies and second on those concerning the engineering problems associated with the use of aerogels as catalysts.

2.2.1. Other catalytic applications

Armor et al. [51] prepared $Pd–Al_2O_3$, $Ni–SiO_2–Al_2O_3$ and $Ni–Al_2O_3$ aerogel catalysts and checked their efficiency in a test reaction of the selective hydrogenation of nitrobenzene into aniline. Aluminum sec butoxide, tetramethyl orthosilicate and metal acetates were used as precursors. The results were quite different depending on the metal. While Pd catalysts were as effective as other well developed commercial hydrogenation catalysts, those prepared with nickel gave bad performance.

According to the characterization by XPS, the palladium catalysts are reduced during the autoclave treatment, in agreement with results of Astier et al. [6]. Electron microscopy allowed the determination of the size of palladium crystallites. Pd appears as well dispersed particles with diameters in the range of 2.0–4.0 nm. Palladium catalysts prepared as xerogels do not reach the activity level of the aerogels. The textural properties are not as well developed in this case and the metal dispersions are lower. The reasons why nickel aerogel catalysts do not compete in activity with the commercial samples were not studied in detail in ref. [51]. In this case, the level of sample reduction, determined by XPS, is low and further treatment of the catalysts in hydrogen is necessary before running the reaction. The reasons for these differences must be related to the chemical structure of the gel, which depends on the chemistry of the different steps of making the catalysts. Different sol–gel routes should be checked in this case of nickel catalysts.

Willey et al. [52] have prepared and characterized $Fe_2O_3–Cr_2O_3–Al_2O_3$ aerogels. These solids show promising properties for the selective catalytic reduction of NO with NH_3. This reaction is of interest for the elimination of NO in flue gases from stationary sources, as in power plants. The conclusion of this work is that iron and chromium oxides do not show a synergic effect when both are present in the catalysts. The activity of the supported binary oxide system is the result of adding the specific activities of iron and chromium oxides separately. This conclusion is not in good agreement with a former paper of Teichner [53] who suggests that the occurrence of interaction between iron and chromium oxides leads to improved catalysts. In both cases, there is a coincidence on the interest of using this type of catalysts because of their high activities and low deactivation rates.

Colmenares et al. [54] proposed an original application based on the use of UO_2^{2+}-doped silica aerogels as photocatalysts for CO and CO_2 hydrogenation, and hydrocarbon hydrogenolysis reactions at ambient temperature. Visible radiation can produce excitation of the uranyl species which can further activate the reactants. C_1 to C_4 hydrocarbons were the main products starting from a $2H_2:1CO$ mixture. The transparency of these aerogels can be considered as an important advantage for this type of photocatalytic activation with visible radiation.

Fanelli et al. [55] developed $TiCl_4–Al_2O_3$ catalysts for polymerization of ethylene. The polymerization of olefins, and particularly the catalytic production of polyethylenes from ethylene, is one of the main processes in the polymer industry. This is the first paper dealing with titania dispersed on aerogels as polymerization catalysts. Alumina aerogels are grafted with $TiCl_4$ under controlled dry atmosphere. The amount of –OH groups of the alumina can be controlled by means of thermal pretreatment. $TiCl_4$ reacts selectively with surface –OH groups, forming hydrogen chloride. In this way, different Ti loadings can be added to the alumina supports. Aerogels prepared by this method present activities similar to those of conventional $TiCl_4$/tryalkyl aluminum catalysts, although a little lower than those of new $MgCl_2/TiCl_4$ commercial catalysts. Nevertheless, the polymer distribution is shifted, in this case of aerogels, to high average molecular weight polymers which can be of interest for some applications.

The method of preparation used by Fanelli et al. is the first example shown in this paper of the application of a grafting technique for the preparation of sol–gel-based catalysts.

2.2.2. *Engineering problems of aerogel catalysts*

Aerogels are usually obtained as very fine powders or fragile monoliths. These properties are not desirable for the development of industrial catalysts. The inherent interest of the fundamental catalytic properties shown by aerogels have prompted to several authors to study possible solutions to these problems.

Armor et al. [56] have proposed a method of encasing aerogels in a variety of open form supports which are added during the preparation, before the gelling step. The method is described for Pd/SiO_2 and for Cr_2O_3 aerogels using alumina rasching rings, capillary glass, glass or metal tubing, cordierite honeycombs and others. The filled supports are useful for operation in fixed bed catalytic reactors, avoiding problems of high-pressure drops or losses of catalysts which can appear when using conventional fine dusty aerogels.

Chaouki et al. [57] and Li et al. [58] have studied the fluidization of aerogel powders in a gas flow of reagents. In principle, the low density and fine particle size (in the order of microns) obstruct the fluidization of aerogel powders in catalytic reactors. These studies show that above a minimal gas flow velocity aerogel particles form agglomerates and fluidize smoothly and homogeneously. These agglomerates are clusters of the original fixed bed materials with new effective apparent size (in the order of millimeters) and weight. The minimal flow velocity to obtain fluidization depends strongly on the aerogel used. SiO_2, Fe_2O_3–SiO_2 and NiO_2–SiO_2 show important differences in aglomeration. The addition of an inert powder material to the aerogel have proved, in several cases, to improve the flow characteristics of the solid.

A recent work by Fanelli et al. [59] deals with the problem of scaling up the synthesis of alumina aerogels to be used as catalyst supports. With this aim, they used a high-pressure reactor of 814 l capacity with agitation. According to the authors, these runs represent the largest batch-type production ever attempted for an aerogel material. Agitation is required in order to maintain the thermal homogeneity in the reactor vessel. The conclusion of the work points out that the high-speed stirring produces a negative effect on the textural properties of the aerogel. Some improvements in reactor design, such as special stirring systems or internal heating devices, are suggestions proposed in the paper in order to approach small-scale autoclave conditions.

3. Other sol–gel methods relevant in catalysts preparation

Frequent literature references to the use of sol–gel methods other than the aerogel route for the preparation of catalysts or inorganic powders of catalytic interest appear. Some of these papers deal directly with the development of catalytic applications, with the focus on the activity measurements or the characterization of some chemical properties related to catalytic behaviour. Others are focused on material preparation. Occasionally they have been conceived for applications in other areas, but the procedures can be extended to the preparation of catalytic materials. Groups working on catalyst development can take advantage of the work carried out in other areas where sol–gel methods have reached a higher degree of development such as glasses, coating technology and structural or device ceramics.

3.1. Preparation of materials

Most work on this topic has the aim to control crystalline structure, particle shape, texture (specific surface and pore size distribution) or surface chemistry (acidity or degree of hydroxylation). The two methods may be classified as those starting from organic precursors or those based on the use of inorganic salts.

3.1.1. Preparations from organic precursors

López et al. [60] discussed the importance of preparing MgO samples with different degrees of surface hydroxylation in order to obtain a better understanding of the behaviour (activity, selectivity and deactivation) of metal catalysts dispersed on these supports. For that purpose, they prepared MgO starting from magnesium ethoxyde and using a series of different catalysts for the hydrolysis and polycondensation reactions. The control of pH and the thermal treatment allow preparation of magnesia powders with controlled levels of surface –OH groups.

Nishiwaki et al. [61] prepared TiO_2 anatase from titanium isopropoxide in propyl alcohol. Solids were obtained by slowly pouring this solution into distilled water with vigorous stirring. These solids are dried and calcined at 420°C in air. Depending on the concentration of the solutions, the particle sizes can be changed from 40 to 4 nm. The study reveals that the lower the particle size, the greater the surface acidity of the sample. The effect is explained on the grounds of charge imbalance at surface locally formed Ti(1)–O–Ti(2), where Ti(1) and Ti(2) represent Ti atoms in different environments. The smaller the particle size, the higher the surface area and the higher the number of titanium atoms with low coordination numbers that will be present at the surface.

Machida et al. [62] studies catalytic supports for high-temperature applications, such as catalytic combustion for jet engines. The method allows the preparation of supports with more than 10 $m^2\ g^{-1}$ after calcination at 1600°C (more than any other known support at this temperature). This textural stability is explained on the grounds of the formation of a mixed compound $BaO \cdot 6Al_2O_3$. Barium and aluminium isopropoxide are refluxed with iso-propanol under nitrogen. After 5 h, water is added and the precipitate is aged for several hours before drying and calcination. The sol–gel route allows a dispersion of the components at the atomic level, thus favouring the formation of the mixed refractory oxide. Other synthesis methods result in the separated formation of BaO and α-Al_2O_3.

Ribot et al. [63] have recently published an excellent work concerning the preparation of CeO_2 gels and colloids obtained via hydrolysis of modified cerium isopropoxide. The reactivity of Ce(IV) isopropoxide, which is a very moisture-sensitive compound, can be decreased by complexing with acetylacetone. The cerium alkoxide forms a dimer $Ce_2(OPri)_8 \cdot 2HOPr^i$ [I] which depending on the relative amount of acetylacetone can be transformed into $Ce_2(OPr^i)_7 \cdot (Acac) \cdot HOPr^i$ [II], $Ce_2(OPr^i)_6 \cdot (Acac)_2 \cdot HOPr^i$ [III] and $Ce_2(OPr^i)_4 \cdot (Acac)_4 \cdot HOPr^i$ [IV] species. The reactivity of a solution is related to the distribution of these species. If the amount of Acac is high, forms III and IV are predominant resulting in the formation of weakly condensed species that cannot bind to one another. Therefore, no gelation can occur even after a long time. The hydrodynamic size of these species is about the size of a closo hexamer, ~ 1.5 nm. The other limiting case corresponds to a low level of complexation. In this case, form I is dominant, hydrolysis and condensation reactions are very fast and an oxide type network is formed yielding a precipitate. When type II species predominate, weakly branched polymerized species, which can further condense leading to a gel formation, appear. In summary, the control of the amount of complexating agent allows one to select the type of ceria product obtained. All of these ceria varieties can be of interest for catalytic applications, since CeO_2 is one of the systems which currently draw more fundamental and industrial attention.

Carturan et al. [4] proposed a method to prepare catalysts by coating glass microspheres with inorganic oxides obtained from alkoxide solutions. Glass spheres (0.04, 0.08 mm of diameter) are wet with alcoholic solutions of the selected alkoxide $(Al(OBu)_4$, $Ti(OBu)_4$, $Zr(OPr)_4$,

$Mg(OMe)_2$, $Si(OEt)_4$ or $Fe(OEt)_3$). The damp material was exposed to moisture to hydrolyze the alkoxide and dried by slow solvent evaporation followed by heating at 400°C. The final product maintains the spherical geometry of the initial carrier and, when using dilute alkoxide solutions, the single glass pearls do not collapse to aggregates. The mechanical stability of the layer was checked by self-limiting at 1 turn/s for 100 h without appreciable loss of deposited oxide. The specific surface per gram of deposited material is in the order of 200–300 $m^2\,g^{-1}$. The depth of the layer may be estimated ranging from 1 μm in the case of Al_2O_3 to 0.1 μm in the case of TiO_2 coatings. In this way, a very cheap support, glass, can be used to disperse active oxide catalysts. The method is also interesting from the point of view of the design of catalytic reactors, leading to catalysts with good mechanical properties and avoiding diffusion problems which can appear when dealing with pellets of bulk gel materials.

Selective grafting of oxides with alkoxides precursors is another technique used to prepare catalysts. Although this is not properly a sol–gel method, it deals with the same type of precursor. Successive monolayers of vanadia can be grafted on TiO_2 supports by selective reaction of $VO(OPr^i)_3$ with surface –OH groups [64,65], leading to catalysts active for the selective reduction of NO by NH_3.

3.1.2. Preparation from inorganic precursors

As pointed out above, the rare-earth oxides, and particularly CeO_2, are materials of growing interest in heterogeneous catalysis. Matijevic and Hsu [66] have proposed a method to prepare monodispersed colloidal particles of rare-earth oxides starting from inorganic salts, such as chloride or nitrates by reaction with urea in aqueous media at 70°C. pH, temperature and aging time are the factors controlling the particle size and the degree of homogeneity of the powders which can be obtained in this way. For the case of the sesquioxides spherical shape amorphous particles (0.2–0.5 μm) which can be decomposed to the corresponding oxides could be obtained, while in the case of ceria the method yielded crystalline oxycarbonate powders, $Ce_2O(CO_3)_2 \cdot H_2O$, of ellipsoidal shape. The reason for this difference in behaviour lies in the lesser reactivity of Ce^{3+} towards hydrolysis. In order to obtain spherical monodispersed CeO_2 particles, Hsu et al. [67] proposed a method starting from Ce^{4+} salts, such as $Ce(SO_4)_2$ dissolved in sulfuric acid and heated at 90°C; Ce^{4+} is much less basic than Ln^{3+} and undergoes strong hydrolysis to give polymeric species and finally the precipitated oxide. In this way, it was possible to generate uniform-sized CeO_2 particles (30–240 nm) by controlled deprotonation of hydrated Ce^{4+} species (forced hydrolysis). A well crystallized CeO_2 with 19.3 $m^2\,g^{-1}$ could be obtained by this method.

Powell et al. [68] have prepared a CeO_2 crystalline powder by reaction of cerium nitrate with citric acid. After drying in vacuum, an amorphous citrate gel is obtained which can be decomposed at 300°C in air to obtain ceria with a BET surface of 42 $m^2\,g^{-1}$.

Fierro et al. [69] prepared CeO_2 by dropwise addition of a cerium nitrate solution 0.32M to ammonia 0.01M at 65°C. Evolution of NO_2 during precipitation is explained as due to reaction of Ce^{3+} with NO_3^- with formation of NO + Ce^{4+}. NO is converted to NO_2 by air. An amorphous ceria aquagel is obtained in this way which was further decomposed in vacuum by a constant-rate decomposition method. This decomposition technique, operating at very low and constant water vapour pressure, partially avoids collapse of the porous structure of the gel during drying. A crystalline product with 60 $m^2\,g^{-1}$ is obtained. This ceria sample has been used to carry out very interesting studies on metal support interaction for Rh/CeO_2 catalysts [70].

Brittain and Gradeff [71] have studied the preparation of organosoluble CeO_2 from a commercial hydrated oxide containing NH_4NO_3 as impurity. This material was peptized at 90°C with oleic acid in an organic solvent such as benzene, toluene, diethyl ether or hexane. After treatment, an aqueous phase containing the NH_4NO_3 impurities, and an organic phase constituted by a sol of colloidal 5.0 nm CeO_2 particles, with adsorbed oleic acid dispersed in the solvent, could be separated. This type of sol can be of interest as catalysts for fluidized bed operation in solid–liquid systems.

The peptization of gels is a commonly used technique which allows further processing of the sol to obtain definite products. Thus, one method to prepare Al_2O_3 spherical granules to be used as catalysts or supports [72] is the peptization of an aluminium hydroxide gel to form a sol which is dropped in a sphere forming substance containing a coagulant agent such as ammonia. Gel spheres are heat treated at 500–600°C leading to the production of γ-Al_2O_3.

Mercera et al. [73,74] have prepared ZrO_2 powders with high surface area, good thermal and chemical stability, and high mechanical strength. A frequent problem in the preparation of ZrO_2 is production of the metastable tetragonal phase which is easily converted into the monoclinic phase. This transformation favours the collapse of the porous structure of this material. In this work, a sol–gel method allows preparation of a pure high surface are monoclinic ZrO_2 without micropores. Zirconyl chloride was mixed with an ammonia solution 6.7M. The gel obtained was aged for 65 h before filtering and washing until elimination of chlorides. The product was redispersed in ethanol and filtered. After drying at 110°C an amorphous powder was obtained which was further calcined at 450°C for 15 h in air to obtain the desired pure monoclinic powder.

A short review on the sol–gel processing of oxide powers, with emphasis on the inorganic routes, was published by Segal [75].

3.2. Catalytic applications

Several groups of catalysts will be considered in this section: dispersed metals, oxide catalysts, and others.

3.2.1. Dispersed metals

Gómez and co-workers have recently published a series of papers concerning Ru, Pt and Pd dispersed on silica [76–79]. The authors compare the effect of adding the metal before gelling, or by conventional impregnation of a silica gel.

For the case of Ru–SiO_2 systems [76,77], the specific activity in the benzene hydrogenation reaction is not very sensitive to the preparation method. An interesting property of all these catalysts is the low rate of deactivation when compared with the behaviour of Ru dispersed on a commercial SiO_2. It is proposed that Ru can be decorated by SiO_2 patches which are formed during the reduction pretreatment, from non-polymerized $Si(OH)_x$ groups. These patches inhibit coke formation which is assumed to require clean and extensive metal facets. On the contrary, in the hydrogenolysis of n-pentane, the commercial silica support present a lower deactivation than the catalysts prepared from gels. For this reaction deactivation seems to take place through a deep hydrogenolysis which would be particularly favored on dense packed surfaces, while simple splitting of C–C bonds would take place on Ru atoms in more defective positions. If it is assumed that SiO_2 patches are preferentially deposited on the edge and corners of the metal crystallites, the higher deactivation rates observed for the gels would be easily explained in this way.

Gómez and co-workers [78,79] studied the application of IR and UV–VIS spectroscopy to the characterization of catalysts prepared by sol–gel methods. Part of the metal (M = Pt, Pd, Ru) can be inserted into the silica network as Si–O–M, thus leading to metal–support interaction effects different from those of conventionally impregnated catalysts. The difference is reflected in the UV–VIS spectra. The metal excess is deposited on the surface. In general, the surface of the sol–gel catalysts present high levels of hydroxylation.

Tour et al. proposed an original procedure to prepare Pd(0) species dispersed in a gel at ambient temperature [80]. This material proved to be a highly chemoselective and stereoselective heterogeneous hydrogenation catalyst at room temperature. The presence of water in the reaction medium did not inhibit the catalytic properties and the catalyst could be easily dispersed in an organic medium. Since no specific reduction treatment is necessary in any of the preparation steps, the nature of the resulting catalysts can be quite different from others in some of their chemical properties, such as the degree of hydroxylation. 0.05 mol Pd(II) acetate is mixed with tetrahydrofurane (5 ml), water (1 ml) and triethoxysilane (2.50 mmol). The solution darkened and H_2 evolution was detected. After gelation the solvent was removed under vacuum and a glassy black xerogel containing Pd(0) could be obtained. An average Pd particle size of 1.5 nm was determined by electron microscopy. This type of catalysts allows easy recycling. After reaction, the solid is filtered and removal of the solvent by evaporation leads to the pure products. Chemical selectivity is observed in the hydrogenation of alkynes to alkenes and in the hydrogenation of terminal double bonds preserving the inner double bonds of hydrocarbon chains [81]. Some examples of stereoselective behaviour are also shown in ref. [81].

Materials containing uniform nanometer-sized metal particles dispersed in a SiO_2 matrix were prepared by Breitscheidel et al. [82] following a new procedure. In the first step, an originally substituted alkoxysilane of the type $X(CH_2)_3Si(OR)_3$ ($X = NH_2$, $NHCH_2CH_2NH_2$, CN) capable of coordinating metal ions, a metal salt and, optionally, $Si(OR)_4$ were processed by the sol–gel method. The gel was purified calcined in air and reduced with hydrogen. The role of the $(CH_2)_3$ group of the silane is to act as a spacer in order to obtain a good metallic dispersion in the gel network. The method leads to excellent dispersion of metal particles (Ag, Cd, Co, Cu, Ni, Pd, Pt) with uniform sizes even for the case of high metal loadings (5–20%). The final product presents specific surfaces of several hundreds of square meters per gram.

Carturan and co-workers [3,83–85] prepared SiO_2–Al_2O_3–Na_2O gels starting from alkoxides, which were converted into glass beads (0.11–0.13 mm diameter) by thermal treatment at temperatures from 230 to 950°C. The degree of hydroxylation of these glasses was related to the thermal treatment temperature. If these glasses are treated with $Pd(C_3H_5)_2$, a surface palladium complex is formed and one molecule of propane per Pd atom is evolved. If the amount of $Pd(C_3H_5)_2$ is lower than the number of surface –OH groups, Pd reaches atomic dispersion. The surface complex can be reduced with LiH at ambient temperature, thus leading to an atomically dispersed metallic palladium catalyst [83]. This catalyst type has been tested for the hydrogenation of 1-hexene dissolved in tetrahydrofurane [83] and for the selective half hydrogenation of phenylacetylene [3]. The method was extended to the preparation of supported PdPt alloy catalysts.

Ueno and co-workers have prepared Fe–SiO_2 catalysts by a sol–gel method starting from $Fe(NO_3)_3$ dissolved in ethyleneglycol and tetraethoxisilane [86,87]. After this mixture is reacted for 2 h at 80°C, water is added to the system and gelation takes place. Samples are further calcined in air at temperatures selected to obtain oxide materials. The catalysts can be reduced in hydrogen at 450°C to obtain metallic iron particles. The catalyst is compared with others prepared by impregnation of silica. In the oxide samples, Fe can be present as FeO, Fe_3O_4 or Fe_2O_3. An EXAFS study of these catalysts shows that, in the impregnated samples, iron is present with Fe_2O_3-like structure while, for the sol–gel samples, iron shows a Fe_3O_4-like structure. For 10% metal loading samples, the average size of the iron particles after calcination at 600 or 1000°C is about 6 or 12 nm, respectively. This level of dispersion is remarkable for iron catalysts because of the tendency towards sintering of this metal. These iron catalysts can be used for ammonia synthesis, Fischer–Tropsch and water gas shift reactions.

3.2.2. Oxide catalysts and supports

Gel materials have been used as photocatalysts for the degradation of organic wastes at room temperature [88,89]. A recent example of this type of application, is the photocatalytic degradation of 3-chlorosalysilic acid over TiO_2 membranes [89]. The selected halogenated organic compound can be considered as a model of similar substances which present severe environmental pollution risks, such as dibromoethane, trichloroethylene, chlorobenzenes or chlorophenols. Sabate et al. [89] have designed a continuous-flow reactor in which the catalyst, TiO_2, is supported on a glass tube. The coating procedure was carried out as follows. A solution of titanium tetraisopropoxide in isopropanol was rapidly mixed with water at room temperature. After 0.5 h reaction, a gel is obtained. This hydroxide gel is peptized with HNO_3 to form a highly dispersed stable colloidal solution. A glass tube is immersed in the colloidal sol for 30 s. It was then withdrawn at a controlled slow speed, dried at room temperature for 1 h, and calcined at 400°C for 3 h. Eight successive layers of TiO_2 were deposited in this way, thus obtaining a TiO_2 anatase membrane with a total thicknesses of 1.3 μm. Degradation of the 3-chorosalysilic acid with bubbling air led to the formation of HCl and CO_2 without significant deactivation with time on stream.

Polymerization reactions on gel catalysts have also been reported [90–92]. Conway et al. prepared chromia dispersed on a silica–titania cogel for ethane polymerization [90,91]. CrO_3 can be stabilized on silica through the formation of Si–O–Cr bonds, while pure chromia would decompose at low temperature. The controlled addition of titania to the support can induce changes in the electronic environment of chromium ions thus favouring a higher selectivity towards lower average molecular weight polymers. Catalysts were prepared by co-precipitation of sodium silicate and titanium tetrachloride in sulfuric acid solution. After 4 h of aging at 100°C, an aquagel was formed. This gel, after drying in air at 100°C, was impregnated with chromium acetylacetonate in ethyl acetate, dried in a rotary evaporator and calcined in air at 600°C to obtain 1% chromium loading catalysts. These materials present good catalytic performances in activity, selectivity and low deactivation rates.

Selective oligomerization of n-butenes on amorphous $NiO–Al_2O_3/SiO_2$ catalysts prepared by coprecipitation of nickel and aluminium hydroxides on silica gel has also been recently reported in the literature [92].

Hydrodesulfurization (HDS) reactions are considered of main importance in the petrochemical industry to eliminate sulfur from oils. Commercial HSD catalysts are usually constituted by $5\%CoO \cdot 16\%MoO_3$ dispersed on alumina. The simultaneous presence of Co and Mo at the surface of alumina produces a synergic effect, improving the performance of these catalysts. The sol–gel method allows preparation of pure alumina supports, thus avoiding the undesirable effects of impurities. In ref. [93], two sol–gel methods to prepare HDS catalysts have been compared. In the first one, aluminum isopropoxide (AIP) is hydrolyzed in a large amount of water forming a fibrillar aluminium hydroxide; the gel is peptized with a HNO_3 solution giving a clear sol. $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ are dissolved in 1,3-butanediol and stirred with the sol for 1 day. The solvent is evaporated at low pressure and the sample is finally calcined in air at 500°C. In the second case, AIP is dissolved in 1-butanol and Mo and Co precursors are added to the solution. Water is further added and a gel is formed which is further dried and calcined at 500°C. The activity of the first catalyst is about ten times higher than that of the second for the thiopene HDS reaction. Auger spectroscopy measurements on both catalysts can provide an explanation for this difference in behaviour. The deep profiling method demonstrates that, in the first case, Mo and Co oxides are both at the surface, while in the second case significant amounts of cobalt are incorporated into the alumina matrix. In fact, cobalt atoms can easily substitute to aluminum ions in tetrahedral positions of the Al_2O_3 network, thus decreasing the synergic effect between surface cobalt and molybdenum. The first catalyst gives levels of activity similar to commercial HDS catalysts.

Another oxide-catalyzed reaction is the selective catalytic reduction of NO with NH_3. Dispersed vanadia is an excellent catalyst for this reaction. However, V_2O_5 deposited on the surface of a silica support agglomerates easily during the preparation of the catalysts or under reaction conditions. The approach followed by Baiker and co-workers [94,95] consists of immobilizing vanadia in a silica matrix by the sol–gel method. The mixed gel, containing from 0.1 to 50% V_2O_5, was prepared by mixing vanadia and silica diluted sols obtained from vanadyl tri-isobutoxide and silicon ethoxide respectively. The mixed sols were dried at 80°C and calcined at 600°C. In addition to their adequate textural properties, vanadia gels ($< 10\%$ V_2O_5) showed well dispersed vanadium oxide species and high specific activities for the catalytic conversion of NO and NH_3 to $N_2 + H_2O$.

The stability of dispersed vanadia was in all cases higher than that corresponding to the conventional vanadia on silica preparations.

More recently, chromia has been proposed as an alternative catalysts for the $NO + NH_3$ reaction above. In ref. [96] the authors compare the behaviour of amorphous and crystalline chromia for this reaction. All chromia samples were prepared by gelation of a chromium nitrate solution with ammonia. If the addition of ammonia is fast, the final products, after drying and decomposition in hydrogen at 380°C for 3 h, are crystalline materials with BET surfaces of less than 100 $m^2 g^{-1}$. On the contrary, if the addition of ammonia is very slow (6 h or more), the final product is amorphous chromia with BET surface > 200 $m^2 g^{-1}$. Temperature programmed reduction experiments showed that the labile oxygen species on the surface of the crystalline chromia were more readily removed with hydrogen while the higher specific activity was measured on the amorphous samples. This is attributed to the higher density of less labile oxygen species on the amorphous surface.

3.2.3. Other catalytic materials

Silico-aluminates are interesting in catalysis by their acidity which confer catalytic properties in cracking, dehydration, polymerization and isomerization reactions. Several works on silicoaluminates and related materials pepared by sol–gel method have recently appeared [97–101].

Corma et al. [97] described the preparation and characterization of amorphous silica-alumina with 13 and 25 wt% Al_2O_3 to be used as cracking catalysts. The starting reagents were silicon dioxide and aluminum isopropoxide (AIP). The SiO_2 was dissolved in a tetra-alkylammonium hydroxide (TAAOH) and mixed with a solution of AIP dissolved in TAAOH. Gelation takes place by addition of a 1M HCl solution. The gels were dried, calcined at 550°C, further exchanged with NH_4Cl and subsequently calcined at 550°C in order to obtain the acidic form of the silica–aluminas. The resulting materials present surface areas close to 300 $m^2 g^{-1}$ and very narrow pore size distribution, centered at 2.0 nm or pore radii.

Yarlagadda et al. [98] compared 15 wt% Al_2O_3 silica–alumina catalysts synthesized in aqueous and alcohol solvents. In the first case, the selected precursors were sodium silicate and aluminium nitrate, while in the second, tetraethyl orthosilicate and aluminum isopropoxide with ethanol as solvent were used. The second catalysts presents acid sites in higher concentration and of higher strength than the first. Nevertheless, some of these stronger acid sites are easily poisoned by strong chemisorption of water, thus decreasing the reactivity of the catalysts for the conversion of methanol into hydrocarbons.

Reddy and co-workers have recently described the preparation and catalytic properties of a new crystallized titanium silicate (TS-2) [99,100]. A sol, obtained from tetraethyl orthosilicate and tetrabutyl orthotitanate, is allowed ty crystallize under static conditions at 170°C for 8 days. In this case, the resulting catalysts do not present strong acidic properties, but are very efficient in the hydroxylation of aromatic compounds.

Silico-aluminophosphates (SAPOs), including very small amounts of nickel in their structure, have also been prepared by a method which results in production of a crystalline zeolite, with chabazite-like structure [101]. The method is based on the preparation of a gel, starting from SiO_2, aluminum phosphate and $NiCl_2 \cdot 6H_2O$, which is further allowed to crystallize by hydrothermal treatment at 200°C for 36 h. The nickel cations are incorporated into the zeolite framework, thus modifying the acidity of the zeolite and introducing subtle structural changes within the active sites. This catalyst is highly selective for the conversion of methanol to ethene at 250°C (100% selectivity, 90% conversion), while similar catalysts without nickel gave only 30% selectivity in ethane.

One strategy which usually leads to highly selective catalysts for production of fine chemicals is the heterogenization of an homogeneous catalyst. In this approach, starting from a previously tested homogeneous catalyst, it is deposited, linked or encased in a support material in such a way that the properties of the homogeneous catalysts are preserved. The heterogenized catalysts are easier to work up, recovery is also simple, and continuous-flow operation is possible. The surface of the support can contribute to modulate the catalytic behavior through electronic or steric effects [102–105].

The catalytic activity of $Rh(CO)Cl(PPh_2CH_2CH_2SiO_{3/2})\cdot xSiO_2$, prepared by the polycondensation of $Rh(CO)Cl[PPh_2CH_2CH_2Si(OEt)O_3]_2$ with tetraethoxysilane, is compared in ref. [102] with that of the homogeneous compound and with a catalyst prepared by attaching the complex to the surface of a silica gel. The heterogenized catalysts present activity for the same type of reactions as the homogeneous compound: formation of poly- and oligo-silanes from hydrosilanes, CO oxidation and water gas shift reaction. With the solid catalysts these reactions can be carried out under milder conditions.

Venturello and co-workers [103,104] prepared silica gels functionalized with amino groups, which are very selective catalysts for the Knoevenagel condensation. This reaction consists in the formation of a double bond linking an alkane with a carbonylic compound. The catalysts described by these authors, depending on the reaction conditions, can produce the selective condensation of aldehydes in the presence of ketones.

Silica gels treated with thionyl chloride are effective and selective catalysts for thioacetalization reactions of aldehydes [105]. Under the same conditions, ketones do not convert. This difference in reactivity between aldehydes and ketones was successfully utilized for the chemoselective conversion of keto aldehydes into the corresponding dithioacetal with the keto group remaining intact.

Finally, immobilization of biocatalysts in a gel matrix is another type of interesting application of gels in the developing field of biocatalysts. Carturan et al. [106] have recently described a method for the inclusion of biocatalysts into thin layers of SiO_2–gel deposited by dip coating on the surface of glass sheets.

4. Conclusions

In this work we have illustrated, with examples taken from the literature, different ways in which the sol–gel routes can be fruitfully used for the preparation of heterogeneous catalysts. From these examples it is possible to conclude that sol–gel methods have a broad field of applications in catalysis, many of which have only been roughly explored up to the present. We have no doubt that a more systematic work, to be carried out in the near future, will make of sol–gel techniques common tools for the synthesis of new and improved catalytic materials.

The authors thank the CICYT (project PB90-0671) and the Junta de Andalucía for financial support.

References

[1] J. Haggin, Chem. Eng. News Sept. 3 (1990) 30.
[2] R. Landau, AIChE Symp. Ser. 86-274 (1990) 9.
[3] G. Carturan, G. Francchin, V. Gottardi, M. Guglielmi and G. Navazio, J. Non-Cryst. Solids 48 (1982) 219.
[4] G. Carturan, G. Francchin, V. Gottardi and G. Navazio, J. Non-Cryst. Solids 63 (1984) 273.
[5] G.C. Bond, Heterogeneous Catalysis: Principles and Applications, 2nd Ed. (Clarendon, Oxford, 1987).
[6] M. Astier, A. Bertrand, D. Bianchi, A. Chenard, G.E.E. Gardes, G. Pajonk, M.B. Taghavi, S.J. Teichner and B.L. Villemin, in: Preparation of Catalysts, ed. B. Delmon, P.A. Jacobs and G. Poncelet (Elsevier, Amsterdam, 1976) p. 315.
[7] G.M. Pajonk, Appl. Catal. 72 (1991) 217.
[8] S.J. Teichner, G.A. Nicolaon, M.A. Vicarini and G.E.E. Gardes, Adv. Coll. Int. Sci. 5 (1976) 245.
[9] S.J. Teichner, Rev. Phys. Appl. C4, 24 (1989) 1.
[10] H.D. Gesser and P.C. Goswami, Chem. Rev. 89 (1989) 765.
[11] G.A. Nicolaon and S.J. Teichner, Bull. Soc. Chim. France (1968) 1906.
[12] S.S. Kistler, J. Phys. Chem. 36 (1932) 52.
[13] G. Pajonk, M.B. Taghavi and S.J. Teichner, Bull. Soc. Chim. France (1975) 983.
[14] M.B. Taghavi, G. Pajonk and S.J. Teichner, Bull. Soc. Chim. France (1978) I-302.
[15] M.B. Taghavi, G. Pajonk and S.J. Teichner, J. Colloid Interf. Sci. 71 (1979) 451.
[16] J. Chaouki, C. Chavarie, D. Klvana and G. Pajonk, Appl. Catal. 21 (1986) 187.
[17] J. Chaouki, C. Chavarie, D. Klvana and G. Pajonk, Can. J. Chem. Eng. 64 (1986) 440.
[18] M. Astier, A. Bertrand and S.J. Teichner, Bull. Soc. Chim. France (1980) I-191.
[19] M. Astier, A. Bertrand and S.J. Teichner, Can. J. Chem. Eng. 60 (1982) 40.

[20] M. Astier, A. Bertrand and S.J. Teichner, Bull. Soc. Chim. France (1980) I-218.
[21] D. Klvana, J. Chaouki, D. Kusohorsky, C. Chavarie and G. Pajonk, Appl. Catal. 42 (1988) 121.
[22] G.E.E. Gardes, G.M. Pajonk and S.J. Teichner, J. Catal. 33 (1986) 145.
[23] W.C. Conner, G.M. Pajonk and S.J. Teichner, Adv. Catal. 34 (1986) 1.
[24] W.C. Conner, in: Hydrogen Effects in Catalysis, ed. Z. Paal and P.G. Menon (Dekker, New York, 1988) ch. 12, p. 311.
[25] D. Bianchi, G.E.E. Gardes, G.M. Pajonk and S.J. Teichner, J. Catal. 38 (1975) 135.
[26] D. Bianchi, M. Lacroix, G.M. Pajonk and S.J. Teichner, J. Catal. 68 (1981) 411.
[27] M. Lacroix, G.M. Pajonk and S.J. Teichner, Bull. Soc. Chim. France (1981) I-258.
[28] M. Lacroix, G.M. Pajonk and S.J. Teichner, Bull. Soc. Chim. France (1981) I-265.
[29] D. Maret, G.M. Pajonk and S.J. Teichner, Stud. Surf. Sci. Catal. 19 (1984) 347.
[30] A. Muller, F. Juillet and S.J. Teichner, Bull. Soc. Chim. France (1976) 1361.
[31] G. Matis, F. Juillet and S.J. Teichner, Bull. Soc. Chim. France (1976) 1633.
[32] G. Matis, F. Juillet and S.J. Teichner, Bull. Soc. Chim. France (1976) 1637.
[33] G. Centi, F. Trifiro, A. Vaccari, G.M. Pajonk and S.J. Teichner, Bull. Soc. Chim. France (1981) I-290.
[34] M. Fromenti, F. Juillet, P. Meriaudeau and S.J. Teichner, Bull. Soc. Chim. France (1972) 69.
[35] F. Zidan, G.M. Pajonk, J.E. Germain and S.J. Teichner, Bull. Soc. Chim. France (1977) 603.
[36] F. Zidan, G.M. Pajonk, J.E. Germain and S.J. Teichner, Bull. Soc. Chim. France (1977) 1011.
[37] G.M. Pajonk, J. Chim. Phys. 88 (1991) 547.
[38] F. Zidan, G.M. Pajonk, J.E. Germain and S.J. Teichner, Bull. Soc. Chim. France (1977) 1021.
[39] F. Zidan, G.M. Pajonk, J.E. Germain and S.J. Teichner, J. Catal. 52 (1978) 133.
[40] A. Sayari, A. Ghorbel, G.M. Pajonk and S.J. Teichner, Bull. Soc. Chim. France (1981) I-220.
[41] H. Zarrouk, A. Ghorbel, G.M. Pajonk and S.J. Teichner, Bull. Soc. Chim. France (1982) I-71.
[42] H. Zarrouk and A. Ghorbel, Bull. Soc. Chim. France (1981) I-78.
[43] A. Sayari, A. Ghorbel, G.M. Pajonk and S.J. Teichner, Bull. Soc. Chim. France (1981) I-7.
[44] A. Sayari, A. Ghorbel, G.M. Pajonk and S.J. Teichner, Bull. Soc. Chim. France (1981) I-16.
[45] A. Sayari, A. Ghorbel, G.M. Pajonk and S.J. Teichner, Bull. Soc. Chim. France (1981) I-24.
[46] A. Sayari, A. Ghorbel, G.M. Pajonk and S.J. Teichner, Bull. Soc. Chim. France (1982) I-39.
[47] S. Abouarnadasse, G.M. Pajonk, J.E. Germain and S.J. Teichner, Appl. Catal. 9 (1984) 119.
[48] M. Rahman, R.J. Wiley and S.J. Teichner, Appl. Catal. 36 (1988) 209.
[49] M. Rahman, R.J. Wiley and S.J. Teichner, Rev. Phys. Appl. C4, 24 (1989) 7.
[50] S. Abouarnadasse, G.M. Pajonk, J.E. Germain and S.J. Teichner, Stud. Surf. Sci. Catal. 41 (1988) 371.
[51] J.N. Armor, E.J. Carlson and P.M. Zambri, Appl. Catal. 19 (1985) 339.
[52] R.J. Willey, H. Lai and J.B. Peri, J. Catal. 130 (1991) 319.
[53] R.J. Willey, J. Olmstead, V. Djuhadi and S.J. Teichner, Mater. Res. Soc. Symp. Proc. 111 (1988) 359.
[54] C. Colmenares, M. Connors, C. Evans and R. Gaver, Eur. J. Solid State Inorg. Chem. 28 (1991) 429.
[55] A.J. Fanelli, J.V. Burlew and G.B. Marsh, J. Catal. 116 (1989) 318.
[56] J.N. Armor, E.J. Carlson and P.M. Zambri, Appl. Catal. 19 (1985) 327.
[57] J. Chaouki, C. Chavarie, D. Klvana and G. Pajonk, Powder Tech. 43 (1985) 327.
[58] H. Li, R. Legros, C.M.H. Brereton, J.R. Grace and J. Chaouki, Powder Tech. 60 (1990) 121.
[59] A.J. Fanelli, S. Verma, T. Engelmann and J.V. Burlew, Ind. Eng. Chem. Res. 30 (1991) 126.
[60] T. López, I. García-Cruz and R. Gómez, J. Catal. 127 (1991) 75.
[61] K. Nishiwaki, N. Kakuta and A. Ueno, J. Catal. 118 (1989) 498.
[62] M. Machida, K. Eguchi and H. Arai, Chem. Lett. (1986) 1993.
[63] F. Ribot, P. Toledano and C. Sánchez, Chem. Mater. 3 (1991) 759.
[64] M. Schraml-Marth, A. Wokaun and A. Baiker, J. Catal. 124 (1990) 86.
[65] G.C. Bond, J. Pérez-Zurita, S. Flamerz, P.J. Gellings, H. Bosch, J.G. Van Ommen and B.J. Kip, Appl. Catal. 22 (1986) 361.
[66] E. Matijevic and W.P. Hsu, J. Colloid Interf. Sci. 118 (1987) 506.
[67] W.P. Hsu, L. Rönnquist and E. Matijevic, Langmuir 4 (1988) 31.
[68] B.R. Powell, R.L. Bloink and C.C. Eickel, J. Am. Ceram. Soc. 71 (1988) C-104.
[69] J.L.G. Fierro, J.M. Rojo and J. Sanz, Colloids Surf. 15 (1985) 75.
[70] J. Cunninghan, S.O'Brien, J. Sanz, J.M. Rojo, J.A. Soria and J.L.G. Fierro, J. Molec. Catal. 57 (1990) 379.
[71] H. Brittain and P.S. Gradeff, J. Less-Common. Met. 94 (1983) 277.
[72] Z.R. Ismagilov, M.N. Shepaleta, R.A. Shkrabina and V.B. Venelov, Appl. Catal. 69 (1991) 65.
[73] P.D.L. Mercera, J.G. Van Omman, E.B.M. Doesburg, A.J. Burggraaf and J.R.H. Ross, Appl. Catal. 71 (1991) 363.
[74] P.D.L. Mercera, J.G. Van Omman, E.B.M. Doesburg, A.J. Burggraaf and J.R.H. Ross, Appl. Catal. 57 (1990) 127.
[75] D.L. Segal, J. Non-Cryst. Solids 63 (1984) 183.
[76] T. López, A. López-Gaona and R. Gómez, J. Non-Cryst. Solids 110 (1989) 170.

[77] T. López, A. López-Gaona and R. Gómez, Langmuir 6 (1990) 1343.
[78] T. López, A. Romero and R. Gómez, J. Non-Cryst. Solids 127 (1991) 105.
[79] T. López, M. Villa and R. Gómez, J. Phys. Chem. 95 (1991) 1690.
[80] J.M. Tour, J.P. Cooper and S.L. Pendalwar, Chem. Mater. 2 (1990) 647.
[81] J.M. Tour, J.P. Cooper and S.L. Pendalwar, J. Org. Chem. 55 (1990) 3452.
[82] B. Breitscheidel, J. Zieder and U. Schubert, Chem. Mater. 3 (1991) 559.
[83] C. Carturan and V. Gottardi, J. Molec. Catal. 4 (1978) 349.
[84] G. Cocco, J. Schiffini, G. Strukul and G. Carturan, J. Catal. 65 (1980) 348.
[85] G. Cocco, G. Carturan, S. Enzo and L. Schiffini, J. Catal. 85 (1984) 105.
[86] S. Tanabe, T. Ida, M. Suginaga, A. Ueno, Y. Kotera, K. Tohji and Y. Udagawa, Chem. Lett. (1984) 1567.
[87] T. Akiyama, E. Tanigawa, T. Ida, H. Tsuiki and A. Ueno, Chem. Lett. (1986) 723.
[88] V. Augugliaro, L. Palmisano, M. Schiavello and A. Sclafani, J. Catal. 99 (1986) 62.
[89] J. Sabate, M.A. Anderson, H. Kikkawa, M. Edwards and C.G. Hill, J. Catal. 127 (1991) 167.
[90] S.J. Conway, J.W. Falconer and C.H. Rochester, J. Chem. Soc. Faraday Trans. I 85 (1989) 71.
[91] S.J. Conway, J.W. Falconer and C.H. Rochester, J. Chem. Soc. Faraday Trans. I 85 (1989) 79.
[92] D. Kiessling, G. Wendt, K. Hagenan and R. Schoellner, Appl. Catal. 71 (1991) 69.
[93] K. Ishiguro, T. Ishikawa, N. Kakuta, A. Ueno, Y. Mitarai and T. Kamo, J. Catal. 123 (1990) 523.
[94] A. Baiker, P. Dollenmeier, M. Glinski, A. Reller and V.K. Sharma, J. Catal. 111 (1988) 273.
[95] A. Wokaun, M. Schraml and A. Baiker, J. Catal. 116 (1989) 595.
[96] H.E. Curry-Hyde, H. Musch and A. Baiker, Appl. Catal. 65 (1990) 211.
[97] A. Corma, J. Pérez-Pariente, V. Fornés, F. Rey and D. Rawlence, Appl. Catal. 63 (1990) 145.
[98] P. Yarlagadda, C.R.F. Lund and E. Ruckenstein, J. Catal. 125 (1990) 421.
[99] J.S. Reddy, R. Kumar and P. Ratnasamy, Appl. Catal. 58 (1990) L1.
[100] J.S. Reddy and R. Kumar, J. Catal. 130 (1991) 440.
[101] J.M. Thomas, Y. Ku, C.R.A. Cathow and J.W. Conves, Chem. Mater. 3 (1991) 667.
[102] M. Schubert, C. Egger, K. Rose and C. Alt, J. Molec. Catal. 55 (1989) 330.
[103] E. Angeletti, C. Canepa, G. Martinetti and P. Venturello, J. Chem. Soc. Perkin Trans. I (1989) 105.
[104] E. Angeletti, C. Canepa, G. Martinetti and P. Venturello, Tetrahedron Lett. 29 (1988) 1427.
[105] Y. Kamitori, M. Hojo, R. Masuda, T. Kimura and T. Yoshida, J. Org. Chem. 51 (1986) 1427.
[106] G. Carturan, R. Campostrini, S. Diré, V. Scardi and E. de Alteris, J. Molec. Catal. 57 (1989) L13.