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Catalytic aerogels

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Abstract

A review of the work involving the preparation, characterization and catalytic applications of aerogels and cryogels is given for the period elapsing from 1991 up to now. Environmental catalytic aerogel supports for high-temperature combustion as well as aerogel catalysts for water treatment are described in more detail because of the importance of the need to protect the purity of air and water by catalytic means.

1. Introduction

Catalytic aerogels are solid materials used for heterogeneous catalysis, in both gas–solid and liquid–solid catalyzed reactions. These catalysts primarily result from a two-step preparation method, first a sol-gel step and second a drying step performed under special conditions, i.e., supercritical conditions of evacuation of all liquid phases.

1.1. The sol-gel process

Very recent papers have described the many potential advantages one can have when preparing catalysts in the form of gels: nanoscale solution chemistry, ultrahomogeneous (or heterogeneous) mixtures, high purity control of reactants, very large porosities and specific surface areas [1–3]. Recently, catalytic sonogels have been synthesized using ultrasound instead of mechanical stirring to mix the reactants [4,5]. The sonogel method has been successfully applied to the sol-gel chemistry where it avoids the use of solvents, the pure reactants being mixed by ultrasound sonication [4]. This last process can be considered as an additional parameter of sol-gel preparations of highly divided materials for catalytic applications.

The sol-gel method appears to be a very powerful means for obtaining 'superdivided' solid materials due to the exceptional versatility of the solution chemistry involved in their synthesis. Moreover, combination of sol-gel chemistry with more conventional methods of preparation of catalysts, i.e., precipitation, impregnation chemical vapor phase deposition, ion exchange etc., may well constitute, in the future, new original ways of catalyst preparation of great interest. Taking advantage of the sol-gel procedure, together with classical methods, can lead to some synergistic effects when combined properly.

For complete details of the sol-gel processing see the other chapters of this special issue.

1.2. Importance of the drying step

The drying of a wet gel which is by nature a very porous material, is controlled by two deci-

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sive phenomena: permeability and capillary stress [7]. These phenomena are governed by the Darcy law and the Laplace law, respectively. When porous texture and very high pore surface areas are preferred, it is necessary to preserve the textural properties of the wet gel by adopting appropriate drying methods [8]. Among these methods, the supercritical drying process as well as the freeze-drying method are particularly suited, as described in [9] and [10]. The first drying mode leads to the preparation of aerogels, while the second one yields ‘cryogels’ or freeze-dried gels [8,10]. When the liquids are evaporated from a wet gel, the dried material is called a xerogel or more simply a gel. In general, xerogels do not exhibit as highly developed textures as aerogels and cryogels [3].

The next section deals with the ‘physical’ description of the methods or preparation of aerogels and cryogels.

2. The supercritical and freeze-drying methods

2.1. Physical principles

During ordinary drying by evaporation of liquids from capillaries (pores), due to the surface tension which is always greater than zero, liquid-vapor menisci exist until pores are completely dried (differential capillary stress) and are responsible for pore collapse [7,8]. Therefore, the surface area exhibited by the solid through its pore is very low [3]. In order to avoid the formation of liquid-vapor menisci during the drying step, two physical based methods are available and practical: either drying the wet gel in an autoclave at a temperature T above the critical temperature T_c of the solvents, liquids etc. [9] (supercritical conditions), or drying by subliming the frozen solvents, liquids etc. filling

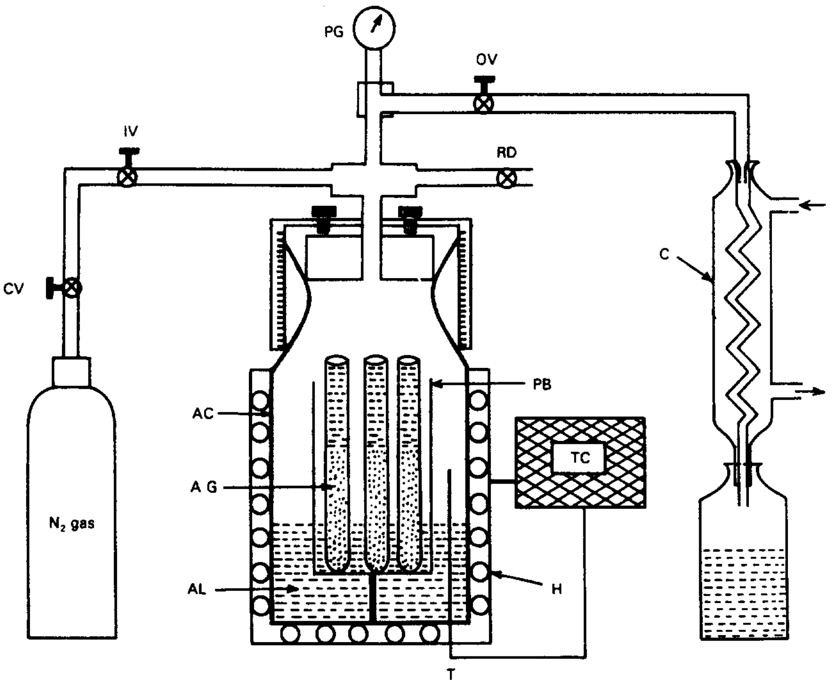
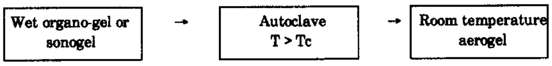
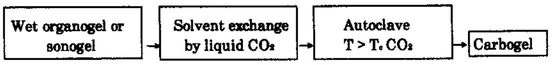


Fig. 1. Schematic cross-section of the autoclave and accessories for supercritical drying of alcogels. CV, N_2 gas cylinder valve; IV, N_2 gas inlet valve; PG, pressure gauge; OV, outlet pressure release valve; RD, rupture disc; PB, Pyrex 250 ml glass beaker; H, heater; C, glass condenser; TC, heater temperature controller; T, thermocouple; AC, autoclave; AG, alcogel; AL, alcohol.



Scheme 1. High-temperature supercritical drying mode.



Scheme 2. Low-temperature supercritical drying mode.

the wet gel [8,10] (freeze drying) in a freeze dryer.

Autoclaves and freeze dryers are readily available from commercial manufacturers.

2.2. High-temperature supercritical drying

Starting with metal–organic precursors as described in [9] and [11] (mainly alkoxides, acetylacetonates, organic salts, etc.), one does not have to wash the wet gel to remove permanent ions released as by products. As the sol-gel process consists of a set of two main reactions (hydrolysis and condensation), water is stoichiometrically reacted (and not used as a solvent because under water-supercritical conditions, all materials are completely peptized and recrystallized in the form of poorly divided materials, i.e., with low S/V ratios where S is the surface area and V the volume of the sample). The currently used solvents are alcohols, such as CH_3OH, C_2H_5OH, C_3H_7OH..., acetone. All of these compounds display relatively high critical temperatures, above 220°C. Scheme 1 illustrates the drying mode according to these high supercritical temperature conditions. Figs. 1 and 2 give the schematic of the autoclave and the diagram showing the temperature and pressure curves versus time on stream, respectively [12].

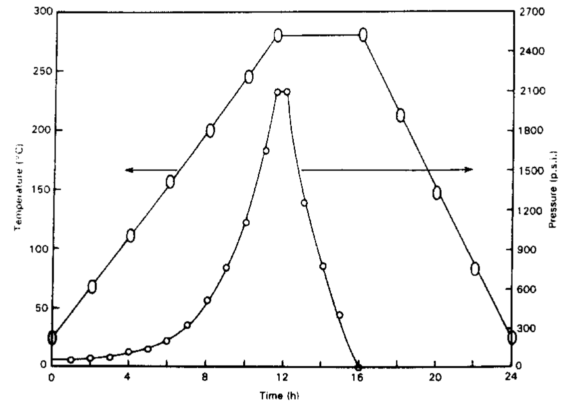


Fig. 2. Temperature and pressure cycles as a function of time for the supercritical process.

Indeed, inorganic precursors in addition to water as solvent can be selected to make the sol-gel step. In the case where water also plays a solvent role, it must be exchanged by an organic liquid before performing the supercritical drying.

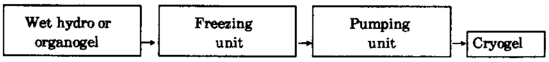
2.3. Low-temperature supercritical drying

In this procedure, advantage is taken from CO_2 which has a very low critical temperature: 31°C. Using this drying process involves a solvent exchange by liquid CO_2 before achieving the drying step. This method gives CO_2 dried aerogels (or carbogels). Scheme 1 must be slightly modified in order to integrate the solvent exchange step as shown in Scheme 2.

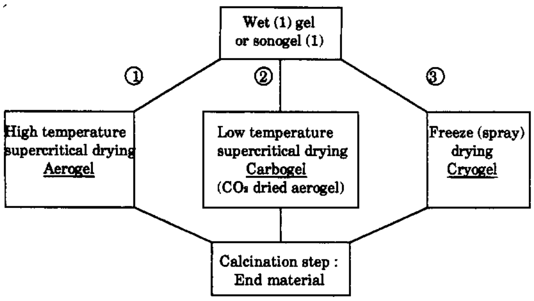
The solvent exchange step can be very much shortened if supercritical CO_2 is directly introduced into the autoclave [13] instead of liquid CO_2.

This supercritical drying process has many interesting features: it is energy saving, very safe, since CO_2 is non-flammable, non-explosive and almost totally chemically inert in the conditions it is employed. By comparison with the high temperature process the CO_2 one is more friendly to the environment and can be considered as a physical process only, while the high-temperature process implies some chemical reactions beside the pure physical evolution during the drying stage [9].

Again, water cannot be used as a solvent because of its very poor solubility in liquid



Scheme 3. Freeze-drying mode.



Scheme 4. Three drying methods leading to highly divided solid catalyst. (1): the gel may be aged or not before going to the drying step.

CO_2. Thus, if a hydrogel is first prepared, a solvent exchange from water to an organic, easily soluble in liquid CO_2, and then a new solvent exchange from the organic to the liquid CO_2 are necessary before drying.

2.4. Freeze-drying or cryogel method

The cryogel or freeze-drying [14] method gives, in principle, the same type of solid materials as those prepared by the aerogel methods [3]. It has the advantages of allowing the use of water as solvent while it does not necessitate drying in a high-pressure vessel (autoclave). Provided that the freezing-step is carried out quickly in order to prevent the solvent from crystallization, one obtains highly divided porous solids [10]. Scheme 3 represents the freeze-drying procedure.

Note that it is important to choose the solvent because the rate of sublimation is strongly dependent on the partial pressure of the frozen solvent. The different methods described above are summed up in Scheme 4.

3. Aerogels as catalytic supports or catalysts

There are few recent, more-or-less extended reports in the literature which give accounts of aerogels as supports of catalysts or catalysts as such [11,15–17].

3.1. Single oxides and carbon

3.1.1. Alumina

High-temperature catalytic combustion requires catalysts and supports which can resist sintering up to 1400°C, i.e., a combustion temperature where NO_x release is strongly reduced as described by Arai and Machida [18] and more recently by Zwinkels et al. [19]. Therefore, relatively abundant studies of the improvement of the thermal textural and structural properties of alumina in the form of aerogel have been published.

Using several spectroscopic types of measurements such as XRD, ^{27}Al MAS–NMR and IR as well as SEM and TEM techniques, Mizushima and colleagues [20–22] prepared different Al_2O_3 aerogels starting with Al-*sec*-butoxide and ethylacetoacetate (etac) as chelating agent in ethanol and a ratio Al-*sec*-butoxide/etac/H_2O equal to 1:1.3:12. Gelation was obtained at 60°C after an aging period of a week. The gels were transformed into a xerogel or into an aerogel (dried in ethanol supercritical conditions at 270°C and 26.5 MPa) or into a 'carbogel' (dried in CO_2 supercritical conditions at 80°C and 15.7 MPa). Both xerogel and 'carbogel' exhibit specific surface areas close to 560 m^2/g while the aerogel showed a lower value 400 m^2/g after drying. A heat treatment was applied to all samples from 600 up to 1400°C for 5 h and XRD patterns demonstrated that at 600 and 800°C, all samples belong to the γ-phase while at 1000°C the 'carbogel' was still in the γ-form, and while the aerogel shifted to the θ-phase and the xerogel became a mixture of α- and θ-structures. Table 1 depicts the crystal forms exhibited at high temperatures for the three dried gels.

It was shown by IR and ^{27}Al MAS–NMR [22] that, at least after firing at 600°C, the 'carbogel' contained pentahedrally coordinated Al^{3+} species which hindered the topotactic transformation phase $\gamma \rightarrow \theta$. It was also clear that the aerogel sample showed a Al^{3+} tetrahedral–octahedral ratio of 1:2.8 smaller than that

Table 1
Crystalline evolution versus temperature (in brackets the BET surface areas in m^2/g from [20])

Temperature (°C)	Carbogel	Aerogel	Xerogel
1100	θ (α) [100]	α [≈ 100]	α [≈ 1]
1200	θ [≈ 8]	θ [≈ 60] [a]	α [< 1]
1300	α [≈ 6]	α [> 10]	α [$\ll 1$]

[a] The same aerogel sample heated at 1200°C for 100 h instead of 5 h, still exhibited a BET surface area of 8.5 m^2/g [23].

of the carbogel which displays a Al^{3+} tetrahedral/pentahedral/octahedral ratio equal to 1:0.1:2.6 [22]. Thus the acidity of the carbogel and aerogel may be different from that of a conventional xerogel or precipitate. An improvement of the structural and textural resistance to heat treatments from 800 up to 1600°C was proposed by Mizushima and Hori [23], who made hexamethylene diisocyanates complex carbogels at the aging step, before drying the wet gel. For instance, BET surface areas were equal for both a simple carbogel and the complex one between 800 and 1000°C, while at 1200°C the carbogel developed 6–7 m^2/g while the complex one exhibited 100 m^2/g. The large difference in S_{BET} was maintained at 1600°C where they showed values close to 0.3 and 20 m^2/g, respectively. XRD patterns disclosed that for the carbogel, the α-phase was recorded at 1200°C, and at 1400°C for the complex one (which still displayed the θ one at 1200°C). TEM pictures of the complex carbogel revealed a needle-like morphology.

Horiuchi et al. [24] prepared an alumina aerogel by first gelling a boehmite sol accordingly to the recipe given by Yoldas [25] from Al-isopropoxide. After peptization by HNO_3, the gel state was obtained by controlling the surface potential of the colloidal particles. The gel was dried under supercritical ethanol (243°C and 6.4 MPa). Decreasing the zeta potential of the boehmite particles during aging, allowed the control of the bulk density of the final materials. Table 2 gives some properties of both a boehmite precipitate and the light aerogel, as a function of the heat treatment and bulk densities.

To explain their results, the authors assumed that for the low bulk density aerogel, a decrease in the neck areas is responsible for its better structural stability.

Ponthieu et al. [26] published a thorough study of the influence of the sol-gel step upon the properties of the alumina aerogels: they started with Al-*sec*-butoxide, different solvents showing different dielectric constants and dipolar moments, such as alcohols, e.g., methanol, 2-butanol, 1-propanol, mixed with aromatics (toluene) and aliphatics, such as pentane, heptane, different Al-*sec*-butoxide/solvent ratios. They noted that the nature of the solvent mixture as well as the dilution of the precursor exerted a conspicuous effect on the BET surface areas. For instance the AB2 sample (unique solvent: 2-butanol) and the ABT3 sample (solvent: a mixture of 2-butanol and toluene) showed BET surfaces at 1200°C equal and close to 25 m^2/g. The structural evolution of these samples with temperature was different for AB2 which showed a γ-phase between 400 and 1150°C where the α-phase was registered, and for ABT3, which exhibited a γ-structure up to 700°C, then between 700 and 1000°C, a δ-structure followed by a θ-structure up to 1100°C and finally the α-phase appeared at higher temperatures. They also concluded that the best samples, from the point of view of BET areas, were synthetized with inert solvents, a polar supercritical fluids and large dilution of the Al-*sec*-butoxide.

Table 2
Physical properties of dense and light aluminas as a function of heat treatment

Alumina	Bulk density (g/cm^3)	α-Phase temperature of formation (°C)	BET surface area heated at 1400°C (m^2/g)
Precipitate	1.1	1170	1
Aerogel	0.06	1400	10

Two papers dealing with alumina cryogels of freeze-dried gels and their principal physical properties conclude that this drying mode [8,9] is also very interesting. The first one by Tsai and Shih [27] reported that after freezing a boehmite sol, the alumina cryogel resulted in the γ-form after calcination at 500°C and exhibited a BET area of 322 m^2/g with a mean agglomerate particle size of 54 nm measured by a laser light scattering unit, while the primary particle dimension was found to be 5 nm and comprised between 5 and 8 nm when estimated by surface area calculation and TEM, respectively.

The second one by Ponthieu et al. [28] described the synthesis and properties of alumina cryogels obtained from aluminium alkoxides–*tertio* butanol–water systems. The cryogel prepared with Al-*sec*-butoxide exhibited a BET area of 350 m^2/g, while the one synthetized from Al-*ter* butoxide had a BET area of 420 m^2/g after heating at 400°C. It is remarkable that the Al-*sec*-butoxide cryogel remained amorphous up to 1000°C [29]. This sample exhibited a BET area of 60 m^2/g after firing at 1150°C.

Great care must be taken in the scale-up of alumina aerogels manufacture as described by Fanelli et al. [30] who found that a high-speed agitator rate is detrimental towards the textural properties of an ex-Al-isopropoxide aerogel made in a 814-liter pilot scale autoclave reactor.

3.1.2. Silica

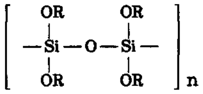
Silica is, along with alumina, one of the most popular supports in heterogeneous catalysis. It is generally considered as a chemically inert carrier, but in certain circumstances, this is not the case [31]; i.e., it can be activated by spillover phenomena.

Recent papers on silica aerogels mainly deal with monoliths of great surface area, porosity and high degree of division. Monomers, such as tetramethylorthosilicate (TMOS) and tetraethylorthosilicate (TEOS), are generally selected as precursors [32–36]; but partially condensed silica from a series of TEOS prepolymers have been developed (polyethoxidisiloxanes)[37,38]. Table 3 gives some recent data on the preparation and surface areas displayed by a large variety of silica aerogel and carbogel samples of interest as supports for heterogeneous catalysts. Additional previous data can be found in [11]. All samples mentioned in Table 3 were degassed at 300°C before surface measurements.

Several silica cryogels have been described in a previous review by the author (see [11] and references therein).

Table 3
Some silica aerogel and carbogel synthesis data

Aerogel (A) and carbogel (C)	S_{BET} (m^2/g)	Precursor	Remark and Ref.
A	333–1183	PEDS [a]	acetogel [37,38] acid catalyzed
C	420–833	PEDS [a]	acetogel [37,38] acid catalyzed
A	500–1200	TMOS	methanogel [35] base catalyzed
A	505–1200	TMOS	methanogel [36] base catalyzed
A	418	TMOS	methanogel [34] base catalyzed
A	145	TMOS	methanogel [34] base catalyzed plus $(CH_3)_4NOH$
A and C	205–806	TMOS	methanogel [33] HF catalyzed
A and C	689–939	TMOS	methanogel [33] neutral medium
A and C	573–939	TMOS	methanogel [33] base catalyzed
A	370–562	TEOS	sonogel [32] acid catalyzed, no solvent necessary

[a] The backbone of the polyethoxydisiloxane (PEDS) can be represented by [37]:  with R = H, C_2H_5 .

$$\left[-\overset{\overset{\displaystyle OR}{|}}{\underset{\underset{\displaystyle OR}{|}}{Si}}-O-\overset{\overset{\displaystyle OR}{|}}{\underset{\underset{\displaystyle OR}{|}}{Si}}- \right]_n$$

3.1.3. Titania

Campbell et al. [39], Schneider and Baiker [40], Brodsky and Ko [41] have synthesized large area TiO_2 aerogels with BET surface areas varying between 220 and 190 m^2/g in the pure anatase form. For more details, see Chapter 5 by Schneider and Baiker in this issue.

3.1.4. Zirconia

Due to its particularly interesting surface properties which, according to Tanabe [42], belong both to the acid-base and redox families, zirconia is very promising as a support and even a catalyst (see section 3.2).

Zeng et al. [43] reported the synthesis of ZrO_2 aerogels starting with zirconium propoxide in solution with isopropyl alcohol and base catalyzed by NH_4OH, which exhibited BET surface areas close to 381 m^2/g. It was also found that the aerogel sample was amorphous at short-range structure, but resembled the monoclinic phase as compared to the tetragonal one. Benedetti et al. [44] showed that the surface area was strongly related to the pH of the sol-gel step, acidic pH gave lower BET values (≈ 260 m^2/g) than basic pH.

A thorough study of ZrO_2 aerogel preparation was published by Ward and Ko [45] who were able to synthesize large surface area ZrO_2 which, at room temperature, had either an amorphous or a tetragonal structure without any additive. After firing at 900°C for 2 h the sample, in the monoclinic phase, still exhibited a BET area of 20 m^2/g.

3.1.5. Other oxides

Maurer and Ko described, in two papers [46], the preparation and properties of niobia aerogels, Nb_2O_5, made by using $Nb(OC_2H_5)_5$ dissolved in butanol. The niobia aerogel was amorphous, has interesting acidic surface properties, a BET area of 190 m^2/g after calcination for 2 h at 500°C and shifted to the low *T* temperature form with a BET area of 5 m^2/g after calcination at 800°C.

Tin oxide aerogels, SnO_2, were prepared by Lu and Chen [47] with an analog method of the Kistler one for silica, i.e., they hydrolyzed $SnCl_4$ instead of tin alkoxide, such as Sn $(OC_4H_9)_4$. This method required a solvent exchange and is time-consuming and tedious [9]. However, they measured BET areas as high as 100 m^2/g and XRD indicated that the samples were in the tetragonal form, moreover the SnO_2 aerogels were not porous systems.

Utamapanya et al. [48] developed a new method for the synthesis of MgO aerogels in a hydrated form by adding toluene to a mixture of $Mg(OCH_3)_2$ and methanol with water. The result was a magnesia aerogel displaying a BET area in excess of 1000 m^2/g as obtained from the autoclave. When dehydrated by heating at 500°C under vacuum, their BET areas decreased in the range of 270–522 m^2/g. The magnesia aerogels were XRD amorphous materials independent of their hydrated or dehydrated state. A freeze-dried magnesia (cryogel) has been described by Tsai and Shih [27] with a BET area of 36.5 m^2/g after calcination at 500°C for 2 h.

A single CuO aerogel was recently prepared in this laboratory [49] which contained mainly Cu^+ ions and developed a BET surface area of 20 m^2/g. The aerogel was synthesized from Cu^{2+} acetate in acetone at 50°C and mixed with aqueous ammonia and the stoichiometric amount of water for hydrolysis. XPS study showed that the three copper species were in the percent ratio $Cu^+/Cu^{2+}/Cu^\circ = 80{:}15{:}5$.

3.1.6. Carbon

Carbon aerogels were obtained by pyrolyzing resorcinol formaldehyde copolymers in an inert atmosphere such as N_2 or CO_2 [50]. First, a resorcinol formaldehyde aerogel is made in the form of a carbogel and subsequently pyrolyzed at high temperature (≈ 1050°C). Depending on their chemical composition, carbon aerogels pyrolyzed in N_2 exhibit BET areas in the range of 659–776 m^2/g, although when pyrolyzed in CO_2, their surface areas increased to the 1225–1320 m^2/g range. Moreover, these carbon aerogels are electrically conductive, their electrical resistivity is lower than 40 mΩ cm, display very large volumetric surface areas in excess of 500 m^2/cm^3. Thus they are very promising candidates for electrocatalyst electrode synthesis. These carbon aerogels can be synthesized in the form of monoliths, films or microspheres.

3.2. Composite mixed oxides

In this section, titania-based catalysts or oxides will not be described since they are the topic of a chapter written by Schneider and Baiker in this issue.

3.2.1. Alumina-based composites

One of the most interesting and recent applications of the aerogel method in alumina composites is the synthesis of barium hexa-aluminate for high-temperature hydrocarbon combustion catalysts for gas turbine (methane combustion) [18,19].

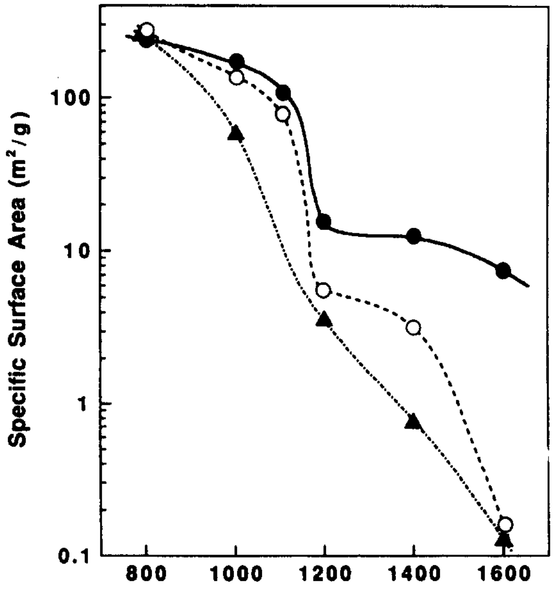


Fig. 3. Specific surface areas of the $BaO \cdot 6Al_2O_3$ aerogel prepared from double alkoxide, alumina aerogel, and $BaO \cdot 6Al_2O_3$ xerogel fired at 800, 1000, 1200, 1400 and 1600°C for 2 h. The solid circles (●) represent the $BaO \cdot 6Al_2O_3$ aerogel, the open circles (○) the alumina aerogel, and the solid triangle (▲) the $BaO \cdot 6Al_2O_3$ xerogel.

Table 4
Crystal phases of barium hexa-aluminate aerogel prepared in the CO_2 extractor and autoclave, fired at temperatures of 800, 1000, 1200, 1400 and 1600°C for 5 h

Temperature (°C)	CO_2 extractor	Autoclave
As-dried	amorphous	$BaCO_3$
800	amorphous	$BaAl_2O_4$
1000	amorphous	$BaAl_2O_4$
1200	barium hexa-aluminate	barium hexa-aluminate [a]
1400	barium hexa-aluminate	barium hexa-aluminate [a]
1600	barium hexa-aluminate	barium hexa-aluminate [a]

[a] A slight presence of the α-alumina phase.

Mizushima and Hori [51] used two Ba hexa-aluminate ($BaO \cdot 6Al_2O_3$) carbogel synthesis methods: a first one from a mixed Ba–Al alcoholate in the presence of diethanol amine and a second one starting with a mixture of Ba metal in 1–3 butanediol and Al-*sec*-butoxide, and addition of a chelating agent ethylacetoacetate. Fig. 3 shows the influence of the heat treatment temperature on the BET surface area for the Ba–Al alkoxide synthesis.

XRD analysis showed that the $Ba_{0.6}$ Al_2O_3 was present at temperatures higher than 1200°C, while no $Ba_{0.6}$ Al_2O_3 phase was detectable below 1200°C. Table 4 shows the structure evolution of the aerogel and carbogel as a function of the temperature treatment. This last structure was present beside the Ba hexa-aluminate for the chelating preparation method.

The superdrying method effect, i.e., aerogel or carbogel, was investigated again by the same authors [52] and their conclusions were that the aerogel method used for the synthesis of Ba hexa-aluminate gave similar results compared to the carbogel method at temperatures > 1400°C (Fig. 4).

Table 5 shows the influence of the introduction of other components into the alumina aerogels on the corresponding BET areas versus heating temperatures. SiO_2, SiC and P_2O_5 were efficient additives at all firing temperatures. XRD showed that the role of SiO_2 and P_2O_5 was to delay the transition to the α-form of alumina. Interestingly, it was also found that at a firing duration of 100 h at 1200°C, the silica aerogel exhibited a BET area of nearly 100 m^2/g against only 15 m^2/g for the pure alumina aerogel [52].

More details concerning the introduction of the SiC whiskers into the alumina aerogel can be found in [53].

Ponthieu et al. [54] introduced hydrated yttrium acetate in an alumina aerogel (1% weight of Y) and found BET areas of the order of 88 and 61 m^2/g when the firing at 1200°C was carried out in N_2 or air, respectively. At 1300°C, these Y-containing samples showed surface areas of the order of 10 m^2/g.

In a certain sense, Komarneni et al. [55] have prepared SiO_2–Al_2O_3 aerogels, counterparts of those described above by Mizushima and Hori [52], because here silica was always the major component (either 0.99 or 0.9 mol%). The 10% mol Al_2O_2 silica exhibited a BET area of 489 m^2/g after calcination at 1000°C for 2 h, while the 1% mole Al_2O_3 silica had a surface area equal to 62 m^2/g in the same conditions.

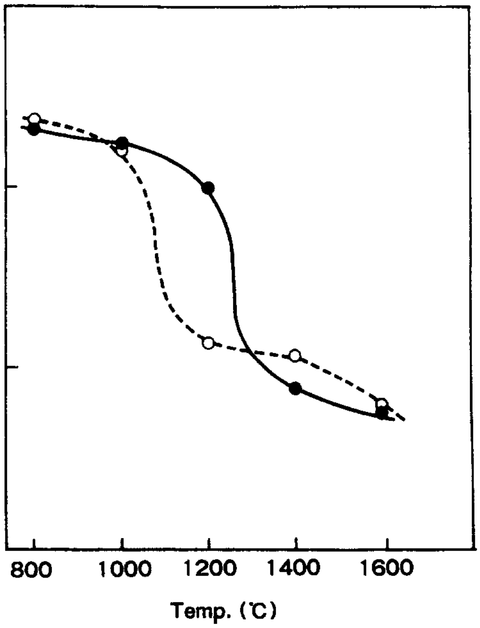


Fig. 4. Specific surface areas of barium hexa-aluminate ($BaO \cdot 6Al_2O_3$) aerogel fired at 800, 1000, 1200, 1400 and 1600°C for 5 h. The solid circles (●) represent $BaO \cdot 6Al_2O_3$ aerogel prepared in the autoclave, while the open circles (○) represent the $BaO \cdot 6Al_2O_3$ aerogel prepared in the CO_2 extractor [52].

Table 5
Specific surface area (m^2/g) of alumina aerogels with the addition of a second component (10 mol%) fired at temperatures of 1200°C for 5 and 100 h and at 1400°C for 5 h

Component	1200°C×5 h	1200°C×100 h	1400°C×5 h
None	88.8	12.9	9.5
Zr	53.4	11.6	8.9
La	46.4	27.3	10.1
P	100.9	56.6	5.2
Ti	12.9	4.1	1.0
SiC [a]	36.1	55.6	11.6
Si	114.3	91.6	12.4
Ba	101.2	10.8	11.3
Mg	59.2	11.3	

[a] SiC whisker at 20 wt%.

In an extended survey of the behavior of binary aluminate and zirconate aerogel oxides, Lowe et al. [56] found that the most resistant material to sintering at high temperatures in the range 1000–1600°C [in the presence of humid air (10% water vapor in volume)] during 4 h was La $Al_{11}O_{18}$ 10 m^2/g at 1600°C, and it even retained a BET area > 10 m^2/g after an exposure during more than 8000 h, i.e., for more than 11 months, at 1250°C in combustion conditions).

A series of alumina aerogels containing ZrO_2, La_2O_3, CeO_2, BaO and TiO_2 have been detailed by Hoang-Van et al. [57]. These binary oxides were prepared either in the form of cogels (one step) or by impregnation of an alumina aerogel preform and thereafter evacuated supercritically (two steps). The first method led to more developed materials (from 615 to 790 m^2/g) than the second one (from 430 to 530 m^2/g). All aerogels prepared in one step were XRD amorphous.

A very recent paper by Mizushima and Hori [58] described Pd on Al_2O_3–SiO_2 aerogels under two forms: an aerogel and a carbogel. The sol-gel step implied Al-*sec*-butoxide, tetraethylorthosilicate, ethylacetoacetone, water, $PdCl_2$ and pyridine (to complex Pd and prevent its non-controlled reduction [31]). After firing at

1200°C for 5 h the aerogel developed a BET area of 93 m^2/g while that of the carbogel amounted to 69 m^2/g only. They also differ in their respective pore size distribution. The dispersion of Pd on the aerogel (1.2%) was four times than that on the carbogel (0.32%) as measured by CO chemisorption.

A niobia–alumina aerogel containing 25% in weight of Nb_2O_5 was reported by Maurer and Ko [59]. It exhibited a BET area of 454 m^2/g after calcination at 500°C and 28 m^2/g at 1000°C. At 500°C, the material was XRD amorphous and showed γ-Al_2O_3 and Nb Al_2O_4 phases at 1000°C.

Three (Zn, Mg and Ca) alumina aerogel spinels were prepared by Guilhaume and Primet [60] to serve as support for CuO which showed much higher BET areas ($\approx$ 100–227 m^2/g) than their counterparts prepared by conventional impregnation methods ($\approx$ 10–50 m^2/g). Aerogels were also found to develop more heat-resistant textures.

3.2.2. Silica-based composites

The influence of minerals of different morphologies, such as boehmite, kaolinite, montmorillonite and mullite, on the textures of silica-based aerogels was studied by Rutiser et al. [61] for two levels of additives: 10 and 1% in mol. All the composite aerogels retained high surface areas even after firing at 1000°C for 2 or 8 h, while pure silica lost all its BET area ($\approx$ 1 m^2/g in the last case versus more than 250 m^2/g for all binary aerogels).

High surface area Pt/SiO_2 xerogels and aerogels using Pt acetylacetonate, chloride and Pt tetramine nitrate to impregnate or cogel silica, were recently synthesized by Zou and Gonzalez [62] who were able to show that xerogels were superior for promoting high Pt dispersions than aerogels, but inferior in terms of BET areas. The best Pt precursor was Pt acetylacetonate in terms of flexibility.

Silica aerogels doped with Eu, Ce, Tb and uranyl ions VO_2^{++} were prepared by Colmenares et al. [63] and described in a study dealing with the photocatalytic reactions of various gas mixtures (see section 4) yielding hydrocarbons.

Mixed silica–niobia (25% weight of niobia) carbogels as well as silica carbogels impregnated by incipient wetness (niobia ethoxide in hexane) were studied by Maurer and Ko [64,46]. The authors recorded that the impregnated carbogel (surface coverage in niobia: 0.05) exhibited a BET area of 630 m^2/g at 1000°C under an amorphous state, and when the heat treatment was maintained during 48 h, its surface was still 280 m^2/g and retained the amorphous state. Higher surface coverage in niobia (0.10 and 0.25) showed small decreases in surface areas and crystalline structures [54].

In order to get homogeneous ZrO_2–SiO_2 carbogels, Miller and Ko [65] pointed out that it is necessary that the two precursors are equally reactive. Therefore these authors used prehydrolyzed silicon precursor (namely, tetraethylorthosilicate, see also [37]). All prehydrolyzed samples showed better temperature stability than the non-prehydrolyzed carbogels [66]. Miller et al. [66] reported that matching the precursors' reactivities could also be met with tetramethylorthosilicate and zirconium propoxide complexed by acetylacetone.

Three papers described the preparation of TiO_2–SiO_2 gels, in the form of xerogels, aerogels and carbogels, to be employed as catalyst supports with Rh and Ni [5,6,67].

Sonogels as well classical sol-gels were prepared by the same group of authors. Impregnated Rh, Ni or Pt on TiO_2–SiO_2 catalysts were better dispersed than when the metal precursors were cogelled with the support compounds (because of some kind of encapsulation). This is another example of the combination of a sol-gel process with a conventional preparation method of supported catalysts which gives better results than impregnating a xerogel, for instance [5,6]. All BET areas were in the range of 550 m^2/g.

The description of the preparation of a Nb_2O_5–SiO_2 catalyst in the form of a carbogel is given in the already-mentioned paper by

Maurer and Ko [46]. Even after a heat treatment at 800 K, the material retained its amorphous state and a BET area of 390 m^2/g. A mixed as well as a surface oxide were shown by these authors referring to the niobia component.

3.2.3. Zirconia-based composites

Sulfated zirconia catalysts have gained increasing interest as superacid catalysts. Two recent papers described a one-step preparation of ZrO_2–SO_4^{2-} by gelling the Zr precursor with H_2SO_4 directly. One group of authors used zirconium propoxide and the carbogel drying mode [68] while the other one synthesized a Pt–ZrO_2–SO_4^{2-} starting with a mixture of Zr propoxide, H_2SO_4 and H_2PtCl_6 and dried the cogel in the form of an aerogel [69].

Sun and Sermon [70] gave an account of the preparation of Cu-doped ZrO_2 aerogels which showed very good stability after both reduction and reaction in terms of BET surface areas (close to 250 m^2/g for each sample) and their XRD patterns disclosed only an amorphous structure. Here, zirconyl and cupric nitrates were mixed in the presence of KOH in the sol-gel step. Thus, not only organometallic precursors can be used in a sol-gel synthesis operation. The same two authors extended their initial work to CaO-, La_2O_3- or CeO_2-doped ZrO_2 aerogels [71]. Again the hydrogel method (and not the alco- or organo-gel) was selected in this work. The main result was that doping the ZrO_2 increased its thermal stability irrespective of the nature of the three dopants. The aerogels exhibited surface areas of the order of 350 m^2/g and were amorphous. The calcined samples, in air and at 450°C, showed tetragonal zirconia.

3.2.4. Other composite mixed oxides

Iron oxide–chromia–alumina ternary aerogels were prepared by Willey et al. [72] who used chromium and ferric acetylacetonates both dissolved in methanol. Binary chromia–alumina and iron oxide alumina were also synthesized.

The ternary and iron oxide on alumina aerogels had a BET area close to 500 m^2/g while the chromia on alumina one exhibited a lower surface area 366 m^2/g.

A series of mixed Mg–Fe oxides of formula $Mg_x\ Fe_{2-2x}\ O_{3-2x}$ were made out of mixtures of Mg acetate and ferric acetylacetonate [73]. For $x \approx 0.5$ the aerogel has a $MgFe_2O_4$ ferrite type structure, while for $0.66 < x < 0.86$, the structure analysis revealed a spinel-type phase mixed with a Mg–Fe compound and when $x = 0.66$, the solid aerogel was composed of a mixture of the spinel-type and hydrotalcite-like type. The surface areas of these materials were between 20 and 150 m^2/g, depending on the composition and pretreatment applied to the series of mixed aerogels.

$Mg_y\ Zn_{1-y}\ Fe_2O_4$ aerogels were also prepared using zinc acetate dihydrate [74]. The oxides were analyzed by XRD and FTIR (and Raman spectroscopy) and they appeared to consist of stable solution spinels. The more Mg they contained, the higher their BET areas after calcination at 500 and 800°C.

Special attention is given to some freeze-dried perovskites (cryogels) prepared and studied by Kirchnerova et al. [75–77]. A $La_{1-x}\ Sr_x\ CoO_{3-y}$ cryogel prepared by spray freezing (ex nitrates) resulted in an interesting electrocatalyst (x varied from 0.7 up to 0.8) with surface areas of the order of 10 m^2/g [75]. Other perovskites also containing Fe, Ni, Mo and Ni, Ni and Fe, Mn, Mn and Ni are described as substituents to Sr and La [75,77]. When these perovskites cryogels were calcined at temperatures close to 850°C they still retained BET areas of the order of 2 m^2/g [77].

Before looking at the catalytic applications of these materials, it is worth mentioning two important facts: on the one hand all these aerogels or carbogels can be fluidized due to the reduction of the interparticle forces reigning in the powders [78], and on the other hand it has been demonstrated that they can also be used in high velocity fluidized beds as shown by Li et al. [79]. At least, a large number of silica-containing aerogels and carbogels can also be prepared in the form of monoliths.

4. Catalytic reactions with aerogel materials

4.1. Hydrocarbon combustion

Methane combustion is described in recent papers on two groups of aerogel type catalysts: Pd on Al_2O_3–SiO_2 [58], CuO on spinels, Mg Al_2O_4, Zn Al_2O_4 and Ca Al_2O_4 [60]; and on a series of La-substituted perovskite cryogels [77,80]. Table 6 gives some data concerning this catalytic combustion reaction. In this table, the light-off temperature, T, corresponds to a conversion of 20 or 2% as indicated.

An attempt at disclosing the reaction mechanism of combustion on perovskite cryogels was described by Klvana et al. [80]. In the case of the Fe perovskite $La_{0.4}$ $Sr_{0.6}$ $Fe_{0.4}$ $Co_{0.6}$ O_3, a Mars and van Krevelen model fitted the data satisfactorily.

Hoang-Van et al. [81] studied the combustion of propane on Pd-Al_2O_3 aerogels in several pretreatments applied to the catalysts, such as reduction, calcination, calcination and reduction or activation by the reactants stream, influence of the concentration of O_2 in the feed and ageing. Their best results were obtained at 20% conversion for an aerogel precalcined with a stoichiometry of the feed $s=[O_2]$:5 $[C_3H_8]$ (corresponding $T=237$°C).

4.1.1. Oxidative dimerization and epoxidation of cyclic olefins

Pajonk and Manzalji have published data dealing with the coupling of CH_4 in C_2 with N_2O on a series of Pb-based aerogels [82]. Their results are presented in Table 7 which shows two main findings: the xerogel PbO_2–ZrO_2 is less active, but as selective, compared to its aerogel counterpart; and the best catalyst of the whole series is the PbO–MgO aerogel.

Hutter et al. [83] reported high selective epoxidation of cyclic olefins on TiO_2–SiO_2 (see the chapter by Schneider and Baiker in this issue).

4.2. Reactions involving NO abatement: SCR reduction by NH_3, CO, and hydrocarbons

This catalytic conversion of NO (and NO_x) into harmless compounds, such as N_2, is a pivotal process in environmentally applied catalysis with regard to the quality of air.

Two papers by Willey et al. [72,73] depicted the use of ternary iron oxide–chromia–alumina and binary magnesium–iron oxide aerogels in the SCR of NO by NH_3 as well as on chromia–alumina and iron oxide–alumina [72]. It was found with the first group of composite aerogel catalysts that the rate of reaction on the ternary Fe–Cr–Al–O aerogel was simply the addition of the rates of the two corresponding binary ones, i.e., Fe–Al–O and Cr–Al–O, respectively. The ternary aerogel showed a maximum of activity at a conversion of 60% of NO with a large flow velocity of 1008 m^3/h kg at 450°C. N_2O was recorded in one case only with the Cr–Al–O catalyst. The second group of catalysts, consisting a series of Mg–Fe–O spinels, clearly demonstrated that addition of Mg increased the conversion at $T\approx 327$°C when the Mg/Fe atomic ratio changed from 1:2 up to 1:1. A mixed oxide with a Mg/Fe = 0.287 exhibited very particular properties: highest rates and conversion (75.5% at 327°C and the presence of two types of active sites assigned to Fe centers, presumably located in octahedral and tetrahedral Fe^{3+} species [73]). Until now, it seems that only one type of active site has been identified, according to the literature.

Binary aerogels containing Pd and alumina or ceria and a Pd on ceria–alumina were carefully studied in the conversion of NO by CO in the presence of oxygen (stoichiometric mixture) by Hoang-Van et al. [84,87]. Pd deposited either on ceria or alumina were the most active in terms of CO oxidation (50% conversion at ≈ 180°C), while for NO, these authors registered that again the same catalysts led to the lowest 50% conversion temperature, i.e., ≈ 240°C, values very close to those of the three-way catalysts.

Table 6
Temperatures (light off) for CH_4 combustion

Catalysts	T (°C)	Remarks	Ref.
$Pd-Al_2O_3-SiO_2$	350	aerogel	[58]
$Pd-Al_2O_3-SiO_2$	400	carbogel	[58]
$CuO/ZnAl_2O_4$	417	aerogel	[60]
$CuO/CaAl_2O_4$	527	aerogel	[60]
$Cu/MgAl_2O_4$	477	aerogel	[60]
$La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$ [a]	280 [b]	cryogel	[77]
$La_{0.4}Sr_{0.6}Fe_{0.4}Co_{0.6}O_3$ [a]	350 [b]	cryogel	[77]

[a] Values corresponding to the best catalysts from a series of 14 cryogels.

[b] CH_4 conversion: ≈ 2%.

4.2.1. *Nitroxidation of propene and aromatics*

Nitroxidation is a reaction performed with NO instead of a mixture of $NH_3 + O_2$ which is currently used in ammoxidation processes. For more details on nitroxidation, see a review by the author [85].

Zine and Ghorbel [86] described the nitroxidation of *p*-xylene with NO on $Cr_2O_3-Al_2O_3$ aerogel catalysts at 450°C. The main products were *p*-tolunitrile (selectivity 85%) and terephtalonitrile which is the corresponding aromatic dinitrile (selectivity ≈ 10%). The best aerogel catalysts were characterized by $Cr/Cr + Al$ atomic ratios of between 6 and 40%.

Nitroxidation of propene gives acrylonitrile as in the ammoxidation process [85]. Pajonk and Manzalji [87] reported on this nitroxidation over PbO_2-ZrO_2 aerogel catalysts. Table 8 summarizes some of their results for a reaction temperature equal to 400°C [87,88].

From Table 8 it is evident that once again the xerogel catalyst (labeled X) is less active and selective than the aerogel of the same composition.

4.3. *Methane and methanol synthesis*

Colmenares et al. [63] have reacted a syngas mixture $CO/H_2 = 1/2$ in a fluidized reactor contained a UO_2^{2+}-doped silica aerogel photoactivated with a 1000-W Hg–Xe lamp at reaction temperatures from 50 to 100°C. Other rare earth cations were used as dopants too (Er^{3+}, Ce^{3+} and Tb^{3+}). At 90°C under illumination, the uranyl-doped silica aerogel yielded mainly in decreasing % in weight: CH_4, ethylene, ethane and propane. A small quantity of methanol was also detected.

Methanol synthesis was studied on $Cu-ZrO_2$ aerogels by Sun and Sermon [70] with methanol selectivities in excess of 87.5%, and by Bianchi et al. [89] on Cu–Zr–O, Cu–Zn–Zr–O, ZrO_2 and Zn–Zr–O aerogels. They found that ZrO_2 was transformed into a H_2 reservoir by H spillover from associated ZnO and/or CuO [90]. Here ZnO and/or CuO played the role of donor and ZrO_2 that of acceptor [31].

4.4. *C_4 hydrocarbon isomerization reactions*

Niobia-based aerogels display interesting acidic properties as measured both by FTIR (Fourier Transform Infrared) using pyridine [46] and *n*-butylamine titrations [46,64]. The

Table 7
Catalytic properties of supported lead oxide catalysts at 720°C

Catalyst	Total activity in mol g^{-1} s^{-1} × 10^{-7} (and in parenthesis in mol m^{-2} s^{-1} × 10^{-7})	Conversion (%)	Selectivities (%)			
			C_2H_4	C_2H_6	C_3H_8	CO_2
PbO–MgO	184.0 (5.41)	3.8	10	57	2.2	31
PbO_2-ZrO_2	110.0 (0.65)	2.2	4.5	55	0	41
$PbO-Al_2O_3$	88.5 (0.42)	1.8	4.3	58.5	0	37
$PbO-TiO_2$	41.0 (0.42)	0.8	2.6	62	0	36
$XPbO_2-ZrO_2$ [a]	21.0 (0.48)	0.4	0	61	0	39
$PbO-SiO_2$	negligible	–	–	–	–	traces

[a] Xerogel.

Table 8
Catalytic properties for different lead oxide supported with a fixed Pb/M atomic ratio of 0.5

Catalyst	Specific activity for C_3H_6 disappearance (10^{-7} mol g^{-1} s^{-1})	Conversion of C_3H_6 (%)	Selectivities (%)		
			C_2H_3N	C_3H_3N	CO_2
PbO_2–ZrO_2	66.5	2.3	4.7	86	10
PbO–Al_2O_3	16	0.5	0	84	16
PbO–TiO_2	5	0.1	0	75	25
PbO–MgO	103	1.3	9	0	91
PbO–SiO_2	0	0	0	0	100
X PbO_2–ZrO_2	57	0.9	3	79	18

Brönsted acidity developed by the mixed niobia oxide aerogels (Al_2O_3, SiO_2 and titania) was at the origin of their 1-butene isomerization properties, while on pure niobia, Lewis acidity built up together with Brönsted sites [46]. The *cis/trans* butene ratio was found to range between 0.7 and 1.3 at 150°C, suggesting a 2-butyl carbonium ion intermediate.

Pajonk and El Tanany [91] have shown that a ZrO_2 aerogel activated at 430°C in vacuum led to better activity for 1-butene isomerization than activation at lower temperatures. A conversion of 87% was registered for a reaction temperature of 200°C. The *cis/trans* ratio strongly depended upon the reaction temperature as shown in Fig. 5.

Selective poisoning runs with CO_2 and NH_3 were probed in order to gain insight into the active sites. Results indicated that O^{2-} or O^- surface sites were active. Thus a carbanion mechanism is involved.

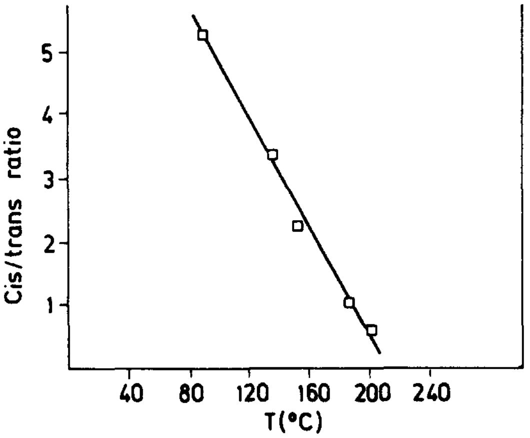


Fig. 5. Variations of the *cis/trans* ratio as a function of the reaction temperature.

Miller et al. [66] and Miller and Ko [65] have underlined the interest in using prehydrolyzed silicon alkoxide to prepare better ZrO_2–SiO_2 carbogels for 1-butene conversion, from the point of view of their activities. The best results were recorded when the ‘prehydrolysis ratio’ selected was the one which attained the reactivities matching between silicon and zirconium precursors [66].

Superacid aerogels were synthesized in a one-step process, in quite the same time by Ward and Ko [68] and Cerrato et al. [69]. In the first case, a ZrO_2–SO_4^{2-} (SZ) cogel was first made and dried to give a carbogel; in the second case, both ZrO_2–SO_4^{2-} and Pt–ZrO_2 – SO_4^{2-} (PSZ) cogels were dried as aerogels. Isomerization of *n*-butane to isobutane in presence of H_2 was the test reaction.

Table 9 gives the intrinsic and specific activities of some superacidic zirconia-based aerogels. Results are given at steady state.

4.5. Hydrogenation and hydrogenolysis reactions

Hydrogenolysis of *n*-butane has been performed on some TiO_2-based aerogels, carbogels and sonogels [5,6,67]. This reaction is described in this issue by Schneider and Baiker.

Besides the isomerization of 1-butene in H_2 on a zirconia aerogel [91], this molecule was also simultaneously hydrogenated into *n*-butane. 1-Butene was converted to 90% at 200°C, the

Table 9
n-Butane isomerization on superacid aerogels

Catalyst	Ai (10^{-9} mol/m^2/h)	As (10^{-6} mol/g/h)	Remarks	Ref.
AZ SO_4 at 280°C (carbogel) [a]	0.67	0.1	20% in sulfate	[68]
PSZ at 250°C	1.79	0.25	1% Pt in weight 6.2% in sulfate	[69]
SZ at 250°C	1.3	0.18	5.5% in sulfate	[69]

[a] AZ SO_4 with only 5% in sulfate was totally inactive.

cis/trans ratio attained 0.6 and *n*-butane was produced with a selectivity of 55.5%. In He, the *cis/trans* ratio measured was again 0.6, showing that H_2 did not modify the isomerization-active sites.

A series of Ni–Al_2O_3 aerogels and carbogels were studied by Klvana et al. [92] in order to hydrogenate toluene in a fluidized bed at temperatures between 90 and 150°C. The cryogel was obtained in two different ways: one was synthesized with Al-*sec*-butoxide and Ni acetate (like in the case of the aerogel); while a second method involved inorganic precursors: Al, Ni and nitrates. For example, at 130°C, the conversions of toluene into methylcyclohexane were of 0.4, 0.2 and 0.156 for the aerogel, cryogel (first method) and cryogel (second method), respectively.

Zou and Gonzalez [62] described the catalytic properties of sol-gel Pt–SiO_2 catalysts for the hydrogenolysis of *n*-hexane at 400°C. They compared xerogels and aerogels to more classical catalysts. Impregnation of the silica aerogel as well as ion exchange and also cogelling were carried out to make the catalysts. Different Pt precursors were also tested such as $Pt(AcAc)_2$, H_2PtCl_6 and $Pt(NH_3)_4(NO_3)_2$. In all cases, the metal dispersion was lower on the aerogels than on xerogels. Ion exchange gave higher Pt dispersion too ($\approx$ 25% measured by H_2 chemisorption and TEM). The Pt–SiO_2 aerogel behavior was found to be very unusual because of its high selectivity in *n*-hexane hydrogenolysis at low conversion.

4.6. Dehydration of ethanol and methanol

Decanio et al. [93] have synthesized very acidic niobia–silica carbogels as well as pure niobia, which were tested for ethanol dehydration into diethylether and C_2H_4. Using ^{18}O-labeled ethanol, the authors concluded that both Lewis and Brönsted acid type active sites were present at the surface of the niobia-impregnated silica carbogel. The pure niobia carbogel was less acidic than the supported one as shown by TPRS methods.

Dimethylether, which can now be considered as an alternative to diesel fuel, was obtained by the conversion of methanol on a macroporous alumina aerogel at 200°C [94]. Again comparison with similar alumina xerogels demonstrated the far higher activity of the aerogel (20 times on the basis on intrinsic activities). This was

Table 10
Catalytic performances of samples A (aerogel) and X (xerogel) at 200 and 250°C

T (°C)	Catalysts Al_2O_3	As × 10^{-7} mol/g s		Ai × 10^{-10} mol/m^2 s		Selectivities (%)		Phenol conversion (%)
		Anisole	*o*-Cresol	Anisole	*o*-Cresol	Anisole	*o*-Cresol	
200	X	0.4	0.2	0.9	0.5	64	36	0.07
200	A	3.8	1.6	9.3	4	69	31	0.58
250	X	8.3	7.8	17.4	16.5	51	49	1.66
250	A	39.3	59.5	97	146.7	40	60	11

attributed to a higher density of acidic sites present at the surface of the alumina aerogel, since the xerogel and aerogel showed the same activation energies.

4.7. Miscellaneous recent applications

Continuing previous work on the activation of silica aerogel by H_2 spillover [31], it was shown that these high BET area material exhibited very strong acidic sites that are able to crack cumene at only 170°C, whereas classical HY zeolite was active only at a higher temperature ≈ 360°C [95]. Cumene was cracked into propene and benzene besides C and H_2 too.

The same macroporous alumina aerogel involved in the methanol conversion into dimethylether [94] was tested in the reaction of alkylation of phenol into anisole and cresol as main products [96]. Again the catalytic performances were compared to those belonging to an alumina xerogel with the same BET area. The aerogel catalyst exhibited higher intrinsic as well as specific activities as shown in Table 10.

Oligomerization of propene over a SiO_2–Al_2O_3 aerogel was described in a paper by Rouanet et al. [97] which showed that, as expected, pure silica aerogel was inactive at the reaction temperature of 400°C. Reaction products contained two unidentified C9 molecules with one or two unsaturations. Deactivation of the catalyst was also registered within 50 min of reaction.

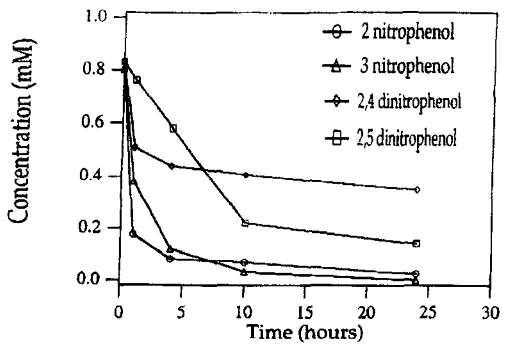


Fig. 6. Degradation of different nitrophenols in air using CuO (1 g/l, 20 m^2/g) under light at pH ~ 2.5.

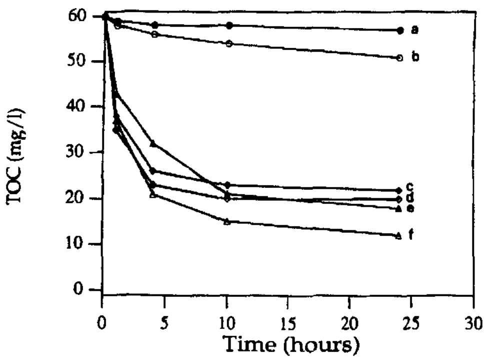


Fig. 7. Degradation of 2-nitrophenol in air using 1 g/l of different catalysts (pH 2.5). a, CuO Fluka (dark); b, CuO Fluka (light); c, Cu(I)O Fluka (dark); d, Cu(I)O Fluka (light); e, CuO aerogel (dark); f, CuO aerogel (light).

Two other recent papers have described the activation of hydrocarbons: the first one dealing with the oxidative dehydrogenation of ethane over a V_2O_5 aerogel [98]; while the second one gave an account of the behavior of a $MgCr_2O_4$ spinel aerogel reactivity towards light hydrocarbons, such as methane, ethane, propene, propane, *n*-butane, 1-butene, benzene and toluene [99]. The first investigation with the vanadia aerogel led to the conclusion that the active sites for the conversion of C_2H_6 into C_2H_4 were those of the higher V oxidation degree, while acidity of the aerogel helped to reoxidize the surface at steady state. Selectivity in ethylene was nearly 90% at 650°C for a corresponding conversion of 9%. The second work put the emphasis on the fact that FTIR spectroscopy identified oxygen containing adsorbed species, in particular alkoxy groups as primary products, which underwent further oxidation into carbonyl and/or carboxylate species experiencing then total combustion in the range of 200–500°C.

Perovskite cryogel electrocatalysts were tested in O_2 evolution from a 5-M KOH solution at ambient temperature as well as at 80°C [75]. The four cryogel electrocatalysts La–Sr–Co–O (two compositions) La–Sr–Fe–Co–O (two compositions) showed Tafel slopes and overpotentials at 80°C and 100 mA cm^{-2} close to 100 mV dc^{-1} and 0.30 μ, respectively.

Nitrophenols could be satisfactorily degraded in abiotic conditions by air in the liquid phase, when in the presence of CuO aerogels of high BET area ($> 20\ m^2/g$) characterized by a composition determined by XPS as follows: 80% Cu^+, 15% Cu^{2+} and 5% Cu°. The reactions were performed in the dark (thermal catalytic conditions) or in the light [100]. Commercial CuO was also tested for comparative investigation. The decrease of the different nitrophenols peaks was followed by HPLC and shown in Fig. 6 with the CuO aerogel catalyst, while in Fig. 7, the decrease in TOC (total organic carbon) is shown for 2-nitrophenol with the CuO aerogel and the commercial Fluka Copper oxide in dark or light conditions.

5. Perspective and conclusions

In the Chemical Engineering Progress issue of June 1995, the associate editor C.M. Caruana [101] titled her article on aerogels ''Aerogels set to take off''. Beyond the many potential applications of this new class of porous materials, catalytic applications appear to be one of the most promising (just behind their applications as thermal superinsulating materials). It is, of course, their unusual massive surface areas which make them so attractive for catalytic reactions. Due to the preliminary step of their manufacture, i.e., the sol-gel step, tailor-made materials can be synthetized in the form of aerogels and cryogels. One must also take into account the relatively fewer number of papers dealing with cryogels, albeit the simplicity and harmless conditions of their preparations.

The flexibility of their chemistry allows these materials to be used as supports and/or catalysts or to be part of a more sophisticated catalytic solid, combining both the sol-gel (and sonogel) and supercritical (or freeze) drying method and other more conventional methods of catalyst preparation.

Carbon aerogels are particularly interesting electrical high surface electrode components for the coming generation of electric cars based on O_2–H_2 fuel cells (and Li–C batteries, for instance) and supercapacitors.

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