ELSEVIER Catalysis Today 52 (1999) 3–13

CATALYSIS TODAY

Some catalytic applications of aerogels for environmental purposes

G.M. Pajonk[1]

Laboratoire d'Applications de la Chimie à l'Environnement, UMR 5634-CNRS-UCB Lyon 1, 43 bd du 11 novembre 1918, 69622, Villeurbanne Cedex, France

Abstract

To protect our environment, catalysts are useful for the treatment of pollutants once they have been generated, or to prevent or at least to minimize their formation. To meet these requirements, very highly divided supports and active phases are necessary for satisfactory results. In particular, nanoparticles such as those obtained by sol–gel chemistry combined with supercritical drying methods ("aerogels") may develop specific catalytic properties from the points of view of textural and thermal qualities. Some examples of gas and liquid phase catalysis such as SCR, deNO$_x$, hydrocarbon combustion and the elimination of nitrophenols and cyanide wastes in water are presented here.

Keywords: Pollutants; Hydrocarbon combustion; Nanoparticles

1. Introduction

Cusumano [1] has put the emphasis on the role of catalytic science and technology in achieving an "environmentally sustainable growth in the 21st century". One very powerful means of synthesizing catalytic materials is the use of sol–gel chemistry, which is capable of providing extremely small particles in the range of nanometers [2–4]. As sol–gel chemistry is a wet process, the gels obtained must be dried in such a way as to conserve their nanostructure in the dried states. An appropriate drying procedure is to evacuate the liquid phase under appropriate supercritical conditions (giving aerogels) or eventually by subliming it using freeze-drying conditions (giving cryogels) [8]. A relatively abundant literature on these matters can be found in [5–8].

NO$_x$ effluents coming from transportation and heating systems include mobile or immobile sources as well as industrial plants represent one of the major pollutants in air. DeNO$_x$ catalytic materials generally are composite solids which are submitted to severe working conditions under which good activity, selectivity and thermostability are properties of paramount importance. In this case, the supports for the active species must exhibit large specific surface areas even at high temperatures in the range of 873 K (normal functioning) up to 1573 K (malfunctioning). The term deNO$_x$ applies to NO$_x$ abatement, such as in the case of car exhaust gas purification as well as the prevention of its formation by the use of catalytic combustors (gas turbines, natural gas engines).

Pollutant molecules found in aqueous environments include both inorganic and organic compounds, especially those containing nitrogen such as mono- and dinitrophenols or the cyanide group, CN.

This paper describes a few examples of each of the characteristic depollution processes listed above.

---

[1] Tel.: +33-472-44-8252; fax: +33-478-94-1995; e-mail: pajonk@univ-lyon.fr

PII: S0920-5861(99)00057-7

2. Aerogels for high temperature combustion of methane

Flameless combustion (or catalytic combustion) systems have many advantages over classical hydrocarbon burners in terms of environmental problems, mainly a significant reduction of NO_x production due to the relatively lower temperatures of catalytic combustion reactions versus the homogeneous ones; a second interesting feature characterizing flameless combustion is that it can be operated in a very large range of air/hydrocarbon ratios in contrast to non-catalytic combustors. The same arguments are also appropriate to methane fueled cars. Only very recent results are given below, previous ones being described in [5–8]. Two series of examples dealing with two families of high temperature resistant supports which develop catalytic activities towards methane combustion, namely pure aluminas and barium hexaaluminates on one hand, and barium hexaaluminates substituted by either Co or Mn (mono substituted) or Co and Mn (di substituted) on the other hand.

2.1. *Pure alumina aerogels (potential supports of active phases)*

A series of 10 samples of alumina aerogels were synthesized under different sol–gel conditions and dried according to two supercritical evacuation methods: at high temperature with respect to the organic liquid phase of the wet gel at around 260°C or at ambient temperature, near 35°C, using liquid CO_2 [8–10]. In the work of Pierre et al. [9] and Elaloui et al. [10] the unique alumina precursor was Al-sec-butoxide while several solvents were used: 2-butanol (B), acetone (A) and finally water (W). In the last case, the excess water was exchanged for methanol, acetone or ethanol through dialysis before applying one of the drying processes. In all gels made in an organic medium, ethyl acetoacetate (etac) was added in the reactant mixture in the presence of acetic acid (c) or nitric acid (n) or ammonia (a). For example, sample AAa60/260 means a gel (first label A) made in acetone (second label A) and etac in the presence of ammonia (a) at 60°C, and finally supercritically dried with respect to methanol at 260°C. Sample AWn85/A/35 means a gel (first A) made in an excess of water (W) in the presence of nitric acid (n) at 85°C, then dialysed in acetone (last A) and finally supercritically dried with respect to liquid CO_2 at 35°C in the autoclave. All aerogels were heat treated in air for 5 h at 400°C, 900°C and 1200°C, respectively, before determining their BET surface areas and XRD patterns. Table 1 shows the results for these materials as well as for their corresponding xerogel counterparts. Xerogels (first label X), made either in water or 2-butanol and aerogels prepared with an excess of water (labelled AW) exhibit the lower resistance to heating treatments at 900°C and 1200°C. The best material after calcination at 1200°C is the aerogel ABc25/35 which exhibits the largest BET surface area. As already described in the literature, water is always detrimental to the state of division of these solids [3,5,7].

Fig. 1 shows the pore size distributions calculated from the corresponding N_2 isotherms recorded at 77 K, for some alumina samples all heat treated in air at 900°C during 5 h [9]. It is clearly seen in this figure that, at least, the two aerogel samples AAa60/260 and AWn85/M/35 exhibit a relatively large mesoporosity centred around a pore radius of 10 nm. The detrimental role of excess water is also underlined not only by the values of BET surface areas gathered in Table 1 but also by the pore volumes (not shown here). This effect of water is also valid for all xerogels as usual [8].

2.2. *Barium hexaaluminate aerogels*

In a very recent paper, Yan and Thompson [11] described the sol–gel synthesis of pure barium or substituted hexaaluminate gels in ethanol, using Al-sec-butoxide, barium ethoxide, etac, Co and Mn nitrates. A small quantity of ammonia and water diluted in ethanol were mixed with the reagents in order to control the sol–gel transition. The gels were supercritically dried with respect to ethanol at 270°C. The aerogels were then heat treated up to 1600°C in a box oven. After calcination at 1200°C for 5 h, XRD analysis indicated that only barium aluminate and hexaaluminate phases were present in non-substituted aerogels; when Co or Mn was introduced in the solids only hexaaluminate was detected. All samples calcined at 1200°C exhibited BET surface areas around 10–16 m^2/g whatever their chemical compositions. Again, it was recorded that the pore sizes of the

Table 1
Nature of phases and specific BET surface areas S_a of alumina xerogels and aerogels (from [9])

	Phases after drying at 400°C (S_a, m^2/g)	Phases at 900°C (S_a, m^2/g)	Phases at 1200°C (S_a, m^2/g)
Xerogels			
XBa70/25	Amorphous (580)	δ-Al_2O_3 (173)	α-Al_2O_3 (<1)
XBn70/25	Amorphous (481)	δ-Al_2O_3 (106)	α-Al_2O_3 (<1)
XWn 85/25	Boehmite AlO(OH) (318)	δ-Al_2O_3 (130)	α-Al_2O_3 (<1)
XWn 25/25	Amorphous (185)	δ-Al_2O_3 (147)	α-Al_2O_3 (<1)
Aerogels hydrolyzed in an organic solvent			
ABa60/260	Boehmite AlO(OH) (577)	γ- or δ-Al_2O_3 (297)	α-Al_2O_3 (10)
ABn60/260	Boehmite AlO(OH) (618)	γ- or δ-Al_2O_3 (270)	α-Al_2O_3 (8)
AAa60/260	Amorphous (507)	γ- or δ-Al_2O_3 (275)	α-Al_2O_3 (12)
AAa50/35	Amorphous (428)	γ- or δ-Al_2O_3 (267)	α-Al_2O_3 (9)
AAn50/35	Amorphous (259)	γ- or δ-Al_2O_3 (204)	α-Al_2O_3 (6)
ABc25/35	Amorphous (369)	κ'-Al_2O_3 (85)	α- + κ'-Al_2O_3 (70)
Aerogels hydrolyzed in excess water			
AWn85M/260	Boehmite AlO(OH) (178)	δ-Al_2O_3 (122)	α- + θ-Al_2O_3 (33)
AWn85/M/35	Boehmite AlO(OH) (415)	γ-Al_2O_3 (179)	α-Al_2O_3 (4)
AWn85/A/35	Boehmite AlO(OH) (471)	γ-Al_2O_3 (179)	α-Al_2O_3 (4)
AWn85/E/35	Boehmite AlO(OH) (449)	δ-Al_2O_3 (169)	α-Al_2O_3 (5)

hexaaluminate aerogel were much larger than those corresponding to the equivalent xerogels, after calcination at 1200°C, though the pore volumes were too very small. The pore diameter distribution was centred at 10 nm.

Methane oxidation catalytic tests were run with the samples calcined at 1200°C between 700°C and 860°C, with a mixture containing 1% of methane in air and with a GHSV equal to 48 000 h^{-1}. The measured light-off temperatures for 10% and 50% conversion of methane led to the ranking as a function of increasing light-off temperatures (see Table 2).

$BaMn_{0.5}Co_{0.5}Al_{11}O_{19-x}$>$BaMnAl_{11}O_{19-x}$>$BaCoAl_{11}O_{19-x}$>$BaAl_{12}O_{19}$>pure hexaaluminate xerogel. Roughly speaking, this ranking follows the same order as that of the BET surface areas as usually found in literature data. The authors drew a number of conclusions from their work: substituted barium hexaaluminate aerogels are better than the simple hexaaluminate, Mn is a better substituent than Co, a synergistic effect is obtained when both Co and Mn are incorporated in the hexaaluminate. There are no major differences from catalytic and textural points of view between Mn-containing solids prepared by either sol–gel or precipitation methods.

3. Aerogels for the selective reduction of NO by NH_3 (SCR)

3.1. *Vanadia–titania aerogels*

It is well known that vanadium–titanium oxides are good catalysts for SCR reactions because they possess high activity and selectivity towards N_2 formation, good resistance to SO_x poisoning while they exhibit inactivity towards the oxidation of SO_2 into SO_3 under the conditions of the SCR reaction [12]. Many reports on aerogel systems based upon doped or undoped vanadia–tiatania can be found in [12–14]. Addition of small amounts of ceria or tungsten oxide [12] or niobia [13] to the base catalysts exerts a positive influence in terms of catalytic activities, i.e. an enhancement of the rates of the SCR reaction.

A short and very good summary of the chemistry and reactivities of vanadium alkoxides can be found in the paper by Schneider et al. [14] which also gives a full account of the sol–gel chemistry used by this group. To avoid vanadia encapsulation phenomena by titania, all catalysts were prepared by a two-step method prone to produce shell-like materials, i.e. comprising an outer layer of vanadia (instead of

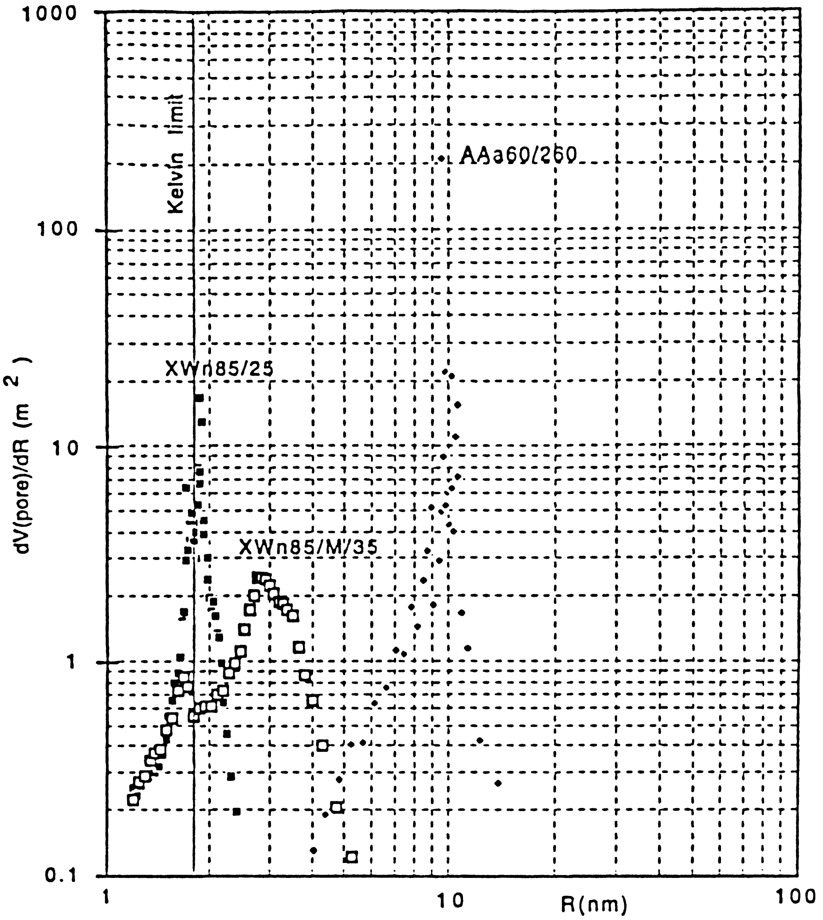

Fig. 1. Pore size distribution of three representative alumina materials (from [9]).

Table 2

Surface areas and methane combustion reaction rates for aerogel-derived and xerogel-derived hexaaluminates following calcination at 1200°C for 5 h (reproduced with permission of Elsevier, Appl. Catal. [11])

Catalyst	Surface area (m^2/g)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)	Reaction rates[b]	
					μmol/g min	μmol/m^2 min
Aerogel-derived materials						
$BaAl_{12}O_{19}$	14.5	710	800	845	<0.1	<0.1
$BaCoAl_{11}O_{19-x}$	13.9	660	760	815	<0.1	<0.1
$BaMnAl_{11}O_{19-x}$	16.3	600	690	755	5.5	0.4
$BaMn_{0.5}Co_{0.5}Al_{11}O_{19-x}$	14.3	585	670	740	10.1	0.7
Xerogel-derived materials						
$BaMnAl_{11}O_{19-x}$	2.0	745	860	–	<0.1	<0.1

[a] Reaction conditions: 1% methane in air; GHSV=48 000 h^{-1}. $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ represent the temperatures at which the methane conversions were 10%, 50% and 90%, respectively.

[b] Reaction rates determined at 550°C under differential conditions (<10% methane conversion).

bulk-like). First a titania gel is prepared from a solution of Ti(IV)tetrabutoxide in methanol which is hydrolysed with water in the presence of nitric acid as catalyst. Thereafter, this gel is redispersed in methanol and V(V)*n*-tripropoxide dissolved in methanol-containing water is added to the suspension with vigorous stirring and then left for 15 h, at room temperature. The composite gels formed were supercritically dried with respect to the alcohol. A very large series of such catalysts (18 samples) were synthesized, differing either in their loadings with respect to vanadia (expressed under as V_2O_5%), the conditions of drying: heating rates, pre-pressure of N_2, and venting rates, hydrolysis catalysts (sulphuric acid instead of nitric acid), gelation and calcination temperatures. The catalytic tests were performed between 370 and 440 K using a reaction mixture comprising of 900 vppm of NO and NH_3 each and 1.8 vol% of dioxygen in Ar. They found that the best aerogel catalyst at a reaction temperature of 423 K, at which only traces of NO_2 were formed was that containing 30% of V_2O_5 (denoted as V30) and calcined at 573 K. A comparison with other V–Ti systems prepared by vanadia grafting on titania P25 or on xerogels (denoted as Ti-3V and Ti gel-2V, respectively), or by a two-step xerogel method (denoted as V Ti gel) or by precipitation methods (denoted as P) gave the following ranking in terms of rates of NO reduction expressed in mol NO per gram of catalyst per second (see Table 3):

V30>V–Ti gel>Ti gel 2V>V–Ti gel>P

The above sequence was explained by the authors on the basis of the higher vanadia loadings which can be achieved by the combined sol–gel/supercritical drying method versus all other ways of making V–Ti catalyst, i.e. more vanadyl surface species V=O (thought to be responsible for the catalytic properties of these SCR systems) are developed per unit mass using the former type of synthesis. Brønsted acidity is suspected to play an important catalytic role in vanadium-containing SCR catalysts [13,14], so niobia was incorporated into the V–Ti aerogel by adding Nb-pentaethoxide into the vanadium methanolic solution. It was found that the triple Ti–V–Nb composite aerogels (20% in vanadia) containing up to 6% of niobia gave the same results if the samples were calcined at temperatures lower than 673 K. A xerogel containing 20% of vanadia and 6% of niobia displayed a greater catalytic activity per gram than its aerogel counterpart at a reaction temperature of 423 K [13].

Willey et al. [12] prepared V–Ti aerogels by cogelling the two precursors, namely Ti propoxide dissolved in 1-butanol and a solution of V acetylacetonate in methanol and dried in the presence of an excess of butanol. They used a Ti/V atomic ratio of 97.5–2.5. A second sample was prepared according a two-step method with the same Ti/V atomic ratio: first a titania aerogel was prepared as such and introduced into the vanadium solution and the thus obtained impregnated titania aerogel was again supercritically dried and calcined at 550°C. SCR tests were run with a mixture containing 2000 ppm of NO and 2500 ppm of NH_3 in the presence of air. The SCR reaction temperatures were varied from 150°C up to 450°C. It appeared that the cogelled catalyst converted 82.9% of NO while the two-step one only 66.5% at a temperature of 450°C at which the maximum conversions were recorded. Addition of ceria (from cerium nitrate or tungsten oxide coming from tungsten hexacarbonyl in solution in methanol) and calcination at 450°C resulted in more active SCR catalytic solids than the binary V–Ti aerogels for both additives. A small amount of Ce (0.1% atomic ratio) increased the activity but when this amount exceeded 1%, the reverse was observed. The ternary V–Ti–W aerogel with 1% (atomic ratio) W showed the highest activity of all the eight tested aerogels, with a NO conversion of 94.6%. Thus very small quantities of ceria or tungsten oxide added to the V–Ti aerogels exerted a beneficial effect on the performances of these ternary catalysts compared to the binary ones.

3.2. *Vanadia–silica aerogels*

An interesting piece of work describing the various V–Si aerogels which can be obtained by using two different supercritical drying modes has been published by Dutoit et al. [15]. One drying mode used was to evacuate the organic liquid phase wetting the gel at its corresponding supercritical temperature which generally corresponds to a high critical temperature (T_c). The other one was to replace the organic liquid of the gel by liquid CO_2 (or even CO_2 in its supercritical state), the CO_2 having a T_c of only 31°C versus for instance a value of 242°C for methanol. Such aspects have been discussed in many papers ([3,16] and

Table 3
Selective catalytic reduction of NO by NH_3 (reproduced with permission of Academic Press, J. Catal. [14])

Aerogel	TOF×10^4 (mol NO/mol V/s)[a]	$r_s \times 10^9$ (mol/m^2 s)	$r_w \times 10^7$ (mol/g_{cat} s)	E_a (kJ/mol)	$T_{50\%}$ (K)
V20STA	1.4	1.6	3.0	59	435
V20STA623	1.4	1.5	3.0	60	436
V20STA673	1.7	2.1	3.6	60	429
V20STA723	0.9	4.8	2.0	57	431[b]
V20ViP	1.4	1.9	3.0	60	437
V20SGT273	1.3	1.7	2.9	60	437
V20SGT323	1.4	1.7	3.2	58	434
V20H2S04	0.4	0.6	0.8	65	468
V0	–	–	–	–	–
V5	0.4	0.1	0.2	66	520[b]
V10	0.7	0.4	0.7	59	469
V30	2.4	4.0	7.8	55	414
V100	0.2	8.7	2.2	44	430[b]
V20HR8	1.4	2.0	3.0	61	436
V20HR30	1.4	1.6	3.2	58	434
V20HR120	1.4	1.8	3.2	61	436
V20PR30	1.4	1.5	3.1	60	436
V20PR12	1.3	1.4	2.8	58	438
V20EM0	1.5	1.6	3.3	60	435
V20NP10	1.5	1.5	3.2	58	435
Ti-3V[c]	2.7	2.0	0.6	43	410
Ti gel-2V[d]	2.7	1.5	1.2	–	–
V–Ti gel[e]	1.0	4.5	6.1	49	–
Pat[c]	1.7	1.2	0.8	43	397

The kinetic data measured at 423 K are represented as turnover frequency (TOF), reaction rate per BET surface area (r_s), reaction rate per gram of catalyst (r_w), and apparent activation energy (E_a). Results of integral reactor tests are represented as temperature necessary to reach 50% NO conversion.

[a] Reaction rate referred to the designed vanadium content (TOF) on the basis of the assumption that all vanadium species are accessible to the reactant gases.

[b] V20STA723: 78 mg_{cat}; V5: 184 mg_{cat}, 0.524 cm^3 (V_{cat}), differential reactor testing GHSV 8400–24 000 h^{-1}; V100: 118 mg_{cat}; otherwise as specified under Experimental.

[c] From [7] with the same experimental conditions except for GHSV (9000 h^{-1}); Ti-3V, vanadia grafted on P25 (Degussa) with 1.8 wt% V_2O_5, 27 m^2/g, 1 g_{cat}; Pat, vanadia–titania prepared by sequential precipitation based on the Mitsubishi patent [10] with 4.8 wt% V_2O_5, 67 m^2/g, 1 g_{cat}.

[d] From [42] with the same experimental conditions: Ti gel-2V, vanadia grafted on titania xerogel with 4.4 wt%, V_2O_5, 86 m^2/g 0.1 g_{cat}.

[e] From [12] with the same experimental conditions: V–Ti gel in situ 513 K, vanadia–titania xerogel prepared by a two-stage sol–gel process with 53 wt% V_2O_5, 139 m^2 g^{-1}, 0.1 g_{cat}.

references therein). Using the high temperature conditions may bring about a series of chemical reactions during the temperature and pressure rises in the autoclave, this corresponds to a type of dynamic supplementary aging step which is particularly difficult to control. Low temperature treatment does not develop such a reactive step. The drying procedure can also have a significant influence on the catalytic activities. Dutoit et al. made their vanadia–silica catalysts by first preparing a prepolymer of silica by reacting TEOS with HCl in ethanol-containing water and thereafter adding either V(V)triisopropoxide in ethanol or V(III)acetylacetonate dissolved in a mixture of acetylacetone and ethanol. A comparison of the rates of NO conversion for three chemically similar solids all containing 10% in vanadia (a xerogel, an aerogel dried at high temperature and one dried at low temperature) showed that the xerogel and the low temperature aerogel were more active than the high temperature aerogel. The influence of the nature of vanadia precursor was illustrated by the very low selectivity to N_2 registered when V(III)acetylacetonate was used to prepare the catalyst. This reflects the observation that this molecule is less reactive than V(V)triisopropoxide [15]. From the results given in [14,15], it can be concluded that under similar reaction conditions, the V–Si aerogels develop higher activities than the corresponding V–Ti aerogels though it is known that V–Ti is better than V–Si in general, (see Table 4).

4. Aerogels for the selective reduction of NO by C_3 hydrocarbons

Two series of publications give an account of the selective reduction of NO with propene and propane. In the first, by Hirashima et al. [17,18] some “classical” oxides in particular alumina and alumina–zirconia, were used with propene as reductant. In the second, propane was used by Zegaoui et al. [19] and Hoang-Van et al. [20] both teams using vanadia–titania catalysts.

4.1. Reduction with propene

Four simple oxide aerogels, titania, vanadia, zirconia and alumina, and one binary oxide alumina–vanadia, were dried at high temperature under supercritical conditions with respect to ethanol. They were all then tested between 200°C and 600°C with a equimolar mixture of 900 ppm of NO and C_3H_6 with 10% dioxygen in He. The corresponding xerogels were also evaluated under the same conditions as for the aerogels. The main conclusion which was that alumina was the most active catalyst at high reaction temperature (80% NO conversion to N_2 at 500°C) while it was the binary one Al–Zr oxide containing less than 10% zirconia which exhibited the highest activity at lower reaction temperatures [18]. Acidity was taken into account to explain the general catalytic results. Further, for the pure alumina and for the zirconia, and zirconia-containing alumina aerogels and xerogels, the corresponding Knudsen diffusion coefficients, D_k, as well the effective diffusivities, D_e, measured for propene at 500°C showed that both diffusion constants decreased for aerogels when the amount of zirconia increased. In the case of the xerogels, these values did not change much with their

Table 4
Textural and structural properties, and kinetic data for SCR of NO by NH_3 (reproduced with permission of Elsevier, Appl. Catal, B [15])

Sample	S_{BET} (S_t) (m^2/g)[a]	(d_p) (nm)[b]	$TOF_{423\ K}$ (NO/V k s)[c]	$TOF_{578\ K}$ (NO/V k s)[c]	$r_{w,423\ K} \times 10^7$ (mol/NO g_{cat} s)[c]	$r_{w,578\ K} \times 10^7$ (mol/NO g_{cat} s)[c]	$T_{X_{NO}=0.25}$ (K)[d]
10 VX	698 (245)	1 (<2)	0.006	0.002	0.07	0.34	–
10 V-LT	840 (53)	9 (17)	0.027	0.06	0.29	0.80	–
10 V-HT	1060 (0)	12 (15)	0.013	0.15	0.15	1.53	587
10 V-HT[a,c]	1103 (18)	12 (25)	0.013	0.15	0.15	1.59	556
20 V-LT	597 (48)	13 (32)	0.030	0.09	0.65	3.19	448
30 V-LT	432 (39)	7 (8)	0.020	0.12	0.66	9.02	453
VS-1	394 (121)	0.4 (<2)	0.082	0.73	0.08	1.85	528

[a] BET surface area: (S_t) denotes specific micropore surface area derived from *t*-plot analysis taken from [26,27].

[b] $d_p = 4V_{p(N_2)}/S_{BET}$: values in parenthesis are the graphically assessed pore-size maxima of the pore-size distribution derived from the desorption branch of the physisorption isotherms [26,27].

[c] Kinetic data measured at 423 and 578 K, respectively. TOF based on total amount of V in catalyst and reaction rate (r_w) referred to mass of catalyst.

[d] Temperature required for 25% NO conversion.

Table 5
Catalytic reduction of NO by propane (reproduced with permission of Elsevier, Appl. Catal. B [19])

Catalyst [a]	C_{NO} (%)	V_{NO} (mmol/h/g V_2O_5)	S_{N_2} (%)[b]	S_{CO_2} (%)[c]
1.6% V/Ti-A	50	223	90	41
2% V/Ti-A	44	160	83	59
4.4% V/Ti-A	89	144.1	87	64
11.3% V/Ti-A	48	31.3	67	56
18.3% V/Ti-A	40	16.1	60	59
1.3% V/Ti-D	40	227	81	48
2.5% V/Ti-D	55	162.8	76	50
3% V/Ti-D	38	93	69	55
5% V/Ti-D	26	38.3	64	67
11% V/Ti-D	33	21.8	67	67
21.6% V/Ti-D	36	12.3	63	66
3% V/Al-A	0	0	–	–
12% V/Al-A	38	23	74	86
20.3% V/Al-A	35	13	56	68
8% V/Ti-E	16	14.6	56	35

Reaction temperature 723 K. Catalyst mass: 0.1 g; pretreatment: 773 K, air, 3 h. [NO]=0.3%; [C_3H_8]=0.3%; balance He.

[a] See Table 2.

[b] $S_{N_2}=[N_2]/([N_2]+[N_2O])$.

[c] $S_{CO_2}=[CO_2]/([CO_2]+[CO])$.

compositions. In all cases, the effective diffusivity constants were higher for the aerogels than for the xerogels, by a factor of 20–60, and it was therefore assumed that the more rapid diffusion was the cause of their better catalytic activities found for these materials compared with those of the xerogels.

4.2. Reduction with propane

Zegaoui et al. [19] prepared their V–Ti and V–Al aerogels with several loadings of vanadia by a two-step method similar to that used by Willey et al. [12] and described briefly above, the aim being to ensure shell-like materials. They reacted the following cation precursors: Al-sec-butoxide in 2-butanol, V(III)acetylacetonate in methanol and Ti-isopropoxide in 2-propanol, drying the resultant gels at high supercritical temperatures. In particular they varied the vanadia loadings of the V–Ti samples from 1.6% up to 18.3%. The reaction conditions were as follows: a mixture of 0.3% of NO and 0.3% of C_3H_8 in helium with no added dioxygen, at 500°C.

The best conversions of NO were obtained with V–Ti aerogels containing less than 4.4% of vanadia. The 4.4% V–Ti exhibited the highest conversion (89%) of all the catalysts tested, together with a good selectivity towards dinitrogen production (87%). The results were also better than those of an impregnated V–Ti P25 and the Eurocat material containing a loading of 8% in vanadia; see Table 5.

Raman spectroscopy and XRD analysis demonstrated that when the amounts of vanadia in the V–Ti aerogels were $\leq$4.4%, the catalysts did not contain crystallized vanadia, i.e. the surface vanadyl groups were composed of VO_x species consisting of monomeric vanadyl or polymeric vanadate species. These conclusions are close to the ones deduced in the SCR reaction conditions presented above, though the two families of catalytic reactions are very different.

5. Aerogels for the treatment of wastes in water

5.1. Copper(I) oxide for mono- and di-nitrophenols degradation

Nitro- and particularly dinitro-phenols are wastes known to be degradable with some difficulty. Bandara et al. [21,22] have tested the degradation of various nitrophenols with a copper oxide aerogel in the dark (thermal catalysis) and in the light (photocatalysis). Air was the oxidant and the nitrophenol solutions were maintained at a pH of 2.5. The catalyst was obtained by reacting copper(II) acetate dissolved in acetone with water containing a trace of ammonia under vigorous stirring. The mixture obtained was placed in an autoclave and supercritically evacuated with respect to an extra amount of methanol. The resulting copper oxide had a BET surface area of 20 m^2/g and contained 80% copper(I) species, 15% copper(II) and 5% copper(0) species as shown by XPS measurements. The aerogel was compared to a commercial copper oxide Fluka with a BET surface of only 2 m^2/g and a very different surface composition: 5% Cu(I) and 95% Cu(II). Photocatalytic experiments were run with a Hanau Suntest lamp (at $\lambda>290$ nm). Fig. 2 shows the results obtained with nitrophenol, with both catalytic materials in the dark and in the light conditions, while Fig. 3 shows the results obtained with the CuO aerogel using several mono- and di-nitrophenols in the light. It is of interest to notice that the copper aerogel was able to convert di-nitrophenols as well as mono-nitrophenols. The reaction products formed were carbon dioxide, dihydrogen, nitrites and nitrates, ammonia and an insoluble polymeric material. Other more conventional strong oxidants such as H_2O_2, $KMnO_4$ and $K_2Cr_2O_7$ were also tested for the degradation of 2-nitrophenol and they were found to be less efficient than the copper aerogel as shown in Table 6 [22].

5.2. *Titania–silica for photocatalytic degradation of ferric cyanide waste*

Ahmed and Attia [23] have studied the influence of adding silica–titania forming binary aerogels for the photocatalytic oxidation of $Fe(CN)_3$ in water. Introduction of some silica resulted in materials which were more transparent, had more developed BET surface areas and less rapid catalytic deactivation than did pure anatase or rutile. The catalyst precursors chosen for the synthesis procedure in this case were tetraethoxisilane, Ti-isopropoxide and nitric acid was used as gelation agent. The high temperature supercritical drying procedure was applied to the alcogels with respect to ethanol at 280°C. Three Ti–Si catalysts

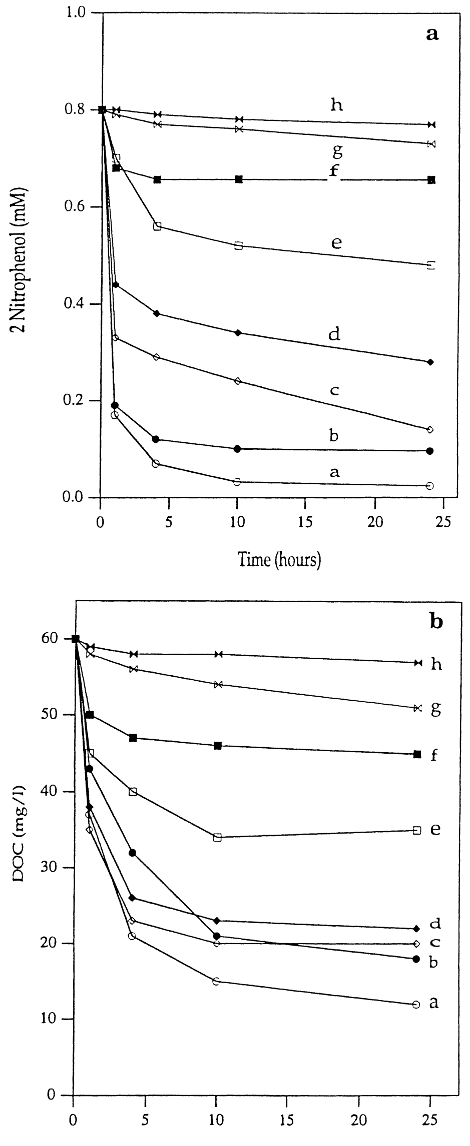

Fig. 2. (A) 2-Nitrophenol degradation profiles with different forms of copper: (a) CuO aerogel, light; (b) CuO aerogel, dark; (c) Cu^{1}O Fluka, light; (d) Cu^{1}O Fluka, dark; (e) CuCl Fluka, light; (f) CuCl Fluka, dark; (g) Cu^{2}O Fluka, light; (h) Cu^{2}O Fluka, dark. (B) DOC (dissolved organic carbon) variation of 2-nitrophenol degradation with different forms of copper: (a) CuO aerogel, light; (b) CuO aerogel, dark; (c) Cu^{1}O Fluka, light; (d) Cu^{1}O Fluka, dark; (e) CuCl Fluka, light; (f) CuCl Fluka, dark; (g) Cu^{2}O Fluka, light; (h) Cu^{2}O Fluka, dark (from [21]).

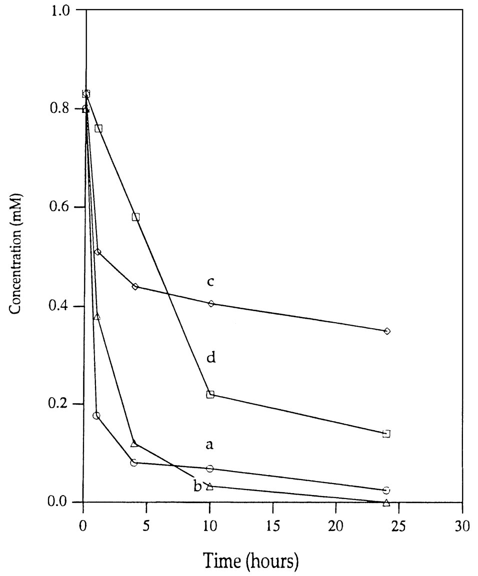

Fig. 3. Degradation of different nitrophenols in air using CuO aerogel (1g/l, 20 m^2/g) under light at pH 2.5: (a) 2-nitrophenol, (b) 3-nitrophenol, (c) 2,4 dinitrophenol, (d) 2,5 dinitrophenol (from [22]).

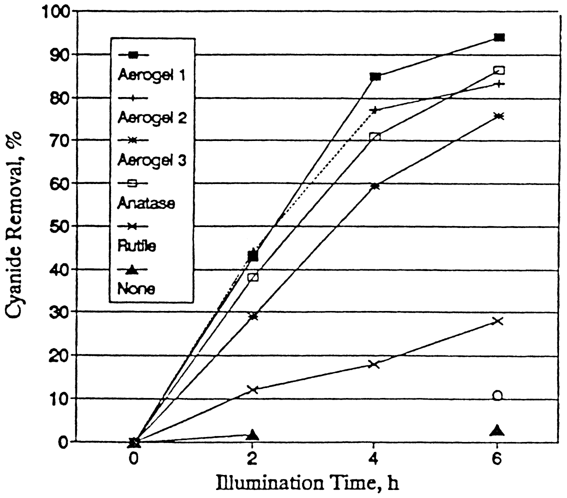

Fig. 4. Photocatalytic oxidation of CN^- in ferric cyanide solution (1000 ppm) using aerogels and particulate photocatalysts ((○) aerogel 1, but without illumination) (with permission of Elsevier, J. Non-Cryst. Solids [23]).

were prepared with the following weight ratios: 1/1, 1/2 and 1/3, respectively. The authors found that the higher the content of silica, the better was the photocatalytic activity. Fig. 4 shows two main results: only photocatalysis (simple photodegradation was not efficient) could oxidize the ferric cyanide and the 1/3 aerogel was better than either the pure anatase or the rutile samples.

6. Conclusions

This very short review of the catalytic behaviours of sol–gel catalysts dried under supercritical conditions clearly indicates the many advantages of using them for the chemical treatments of pollutants of both air and water. Selected examples of such materials illustrated their main advantages: large residual surface areas after heat treatment at high temperatures, important porosities, chiefly in the mesoporous range; and flexibility of chemical composition taking into account that multicomponent catalysts are in general needed, when necessary shell-like solids are easily synthesized. Drying processes were found to play an important role as xerogels (prepared by the evaporation method) and high- and low-temperature aerogels very often display different catalytic properties. Xerogel solids generally exhibit a substantial proportion

Table 6
Oxidation efficiencies towards 2-nitrophenol

	H_2O_2				$KMnO_4$				$K_2Cr_2O_7$				CuO			
	HPLC		DOC		HPLC		DOC		HPLC		DOC		HPLC		DOC	
	D	L	D	L	D	L	D	L	D	L	D	L	L	D	L	D
2-Nitrophenol	85	36	96	94	76	74	97	94	92	94	97	98	31	12	35	22

Percentages of 2-nitrophenol remaining after 8 h of run [22] (D: dark; L: light).

[a] HPLC: high pressure liquid chromatography; DOC; dissolved organic carbon.

of micropores, in particular when acid catalysts are used at the sol–gel stage, but this is not the case with aerogels.

References

[1] J.A. Cusumano, J. Chem. Ed. 72 (1995) 959.
[2] E.I. Ko (Ed.), Sol–Gel Preparation of Catalytic Materials, Catal. Today 35 (1997).
[3] G.M. Pajonk, Heter. Chem. Rev. 2 (1995) 129.
[4] S.J. Monaco, E.I. Ko, CHEMTECH 28 (1998) 23.
[5] G.M. Pajonk, Appl. Catal. 72 (1991) 217.
[6] M. Schneider, A. Baiker, Catal. Rev.-Sci. Eng. 37 (1995) 515.
[7] G.M. Pajonk, Catal. Today 35 (1997) 319.
[8] G.M. Pajonk, Rev. Chim. Appl. 24 (1989) 13.
[9] A. Pierre, E. Elaloui, G.M. Pajonk, Langmuir 14 (1998) 66.
[10] E. Elaloui, A. Pierre, G.M. Pajonk, J. Catal. 166 (1997) 34.
[11] L. Yan, L.T. Thompson, Appl. Catal. A 171 (1998) 219.
[12] R.J. Willey, C.T. Wang, J.B. Peri, J. Non-Cryst. Solids 186 (1995) 408.
[13] M. Schneider, A. Baiker, J. Catal. 150 (1994) 284.
[14] M. Schneider, M. Maciejewski, S. Tschudin, A. Wolkaum, A. Baiker, J. Catal. 149 (1994) 326.
[15] D.C.M. Dutoit, M.A. Reiche, A. Baiker, Appl. Catal. B 13 (1997) 275.
[16] G.M. Pajonk, in: Y.A. Attia (Ed.), Sol–Gel Processing and Applications, Plenum Press, 1994, p. 201.
[17] H. Hirashima, C. Kojima, H. Imai, J. Sol–Gel Sci. Technol. 8 (1997) 843.
[18] H. Hirashima, C. Kojima, K. Kohama, H. Imai, V. Balek, H. Hamada, M. Inaba, J. Non-Cryst. Solids 225 (1998) 153.
[19] O. Zegaoui, C. Hoang-Van, M. Karroua, Appl. Catal. B 9 (1996) 211.
[20] C. Hoang-Van, O. Zegaoui, P. Pichat, J. Non-Cryst. Solids 225 (1998) 157.
[21] J. Bandara, J. Kiwi, C. Pulgarin, P. Peringer, G.M. Pajonk, A. Elaloui, P. Albers, Environ. Sci. Technol. 30 (1996) 1261.
[22] J. Bandara, J. Kiwi, C. Pulgarin, G.M. Pajonk, J. Mol. Catal. A 111 (1996) 333.
[23] M.S. Ahmed, Y.A. Attia, J. Non-Cryst. Solids 186 (1995) 402.