

Aerogel and Xerogel Catalysts Based on θ -Alumina Doped with Silicon for High Temperature Reactions

Aurelien Florin Popa,^[a] Laurence Courthéoux,^[b] Eric Gautron,^[b] Sylvie Rossignol,^{*,[b]} and Charles Kappenstein^[b]

Keywords: Aerogel / Xerogel / Catalyst / Platinum / Alumina

Numerous materials (supports and catalysts) based on alumina have been prepared using the sol-gel process and carbon dioxide supercritical drying. In this work two types of solids, i.e. xerogels and aerogels, were systematically compared and a way of introducing platinum metal with a content of 5% percent by weight was examined. The structural data, the surface area, Pt dispersion and catalytic activity for the decomposition of the propellant were measured for the various samples. The $(\text{Al}_2\text{O}_3)_{0.88}(\text{SiO}_2)_{0.12}$ samples prepared show very interesting porosity values, especially for the aerogel. For this reason, they were chosen as supports for the synthesis of 5 wt% platinum on alumina catalysts. The results presented in this work allowed us to obtain an overall view

of the influence of the preparation mode on the properties of platinum on alumina supported catalysts. The dispersion of the metal phase is directly dependent on the specific surface of the support. A significant value for the surface area implies a large amount of centers for interaction with the metal precursor and, consequently, the appearance of more centres of simultaneous germination. Although aerogels obtained by carbon dioxide supercritical drying always show superior properties compared with xerogels, for catalytic decompositions the xerogels still remain superior.

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Introduction

The sol-gel method represents a way of synthesising materials which display excellent properties suitable for many applications such as catalysis, ceramics and glasses, and nano-materials.^[1] Therefore, numerous catalyst supports or catalysts have been prepared by this procedure which leads to high purity, homogeneous materials with large surface areas. These properties are key factors for the application of these materials.^[2,3] Their properties are comparable and, in some cases, superior to some catalysts prepared using conventional procedures such as co-precipitation or conventional ceramic methods. In particular, we have focussed our interest in recent years on the preparation and evaluation of alumina-based catalysts for applications concerning the decomposition of monopropellants.^[4] For this specific purpose, it is important to obtain catalytic materials or supports displaying high thermal stability (i.e. at 1200 °C or even higher). The selected supports for achieving this purpose are aerogel aluminas^[5] or doped aluminas. In the latter case, the doping element (lanthanum, praseodymium,

barium or silicon) can be introduced during the sol-gel process.^[6–10] Moreover, for catalytic applications, it is generally necessary to add an active phase (a metal phase such as platinum, palladium etc.) to improve the properties.

Numerous authors have used alumina-supported platinum catalysts, prepared generally by the impregnation of commercially available supports. The literature concerning the sol-gel method was less important until the 1990's during which time more papers appeared. Samples have been generally prepared by conventional drying processes (293 to 393 K) leading to xerogels. The use of supercritical drying, generally in carbon dioxide, leads to aerogels but the corresponding reports are much less numerous and focus mainly on pure alumina supports. The first paper concerning a Pt catalyst supported on alumina (aerogel and xerogel) and prepared by the sol-gel method was published in 1993 by Balakrishnan et al.^[11] The alumina precursor used was aluminium tri-*sec*-butoxide $\text{Al}(\text{O-sec-C}_4\text{H}_9)_3$ (ATB) following the work of Yoldas^[12] and the platinum was introduced during the sol-gel transformation using H_2PtCl_6 as a precursor. The supercritical conditions for obtaining the aerogels were $T = 295\text{ °C}$ and $P = 85\text{ bar}$ with methanol. The samples were then treated at 773 K under helium. The main conclusions from this work were: (i) during the treatment, a reduction of the surface area can be observed and (ii) aerogels display a lower Pt metal dispersion in comparison with xerogels of similar loading. In 1998, Cho et al.^[13] prepared the same materials using aluminium tripropoxide Al-

^[a] Alexandru Ioan Cuza University, Faculty of Chemistry, Department of Inorganic Chemistry, 6600 Iasi, Romania

^[b] University of Poitiers, LACCO UMR 6503, Laboratoire de Catalyse par les Métaux, 40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France
Fax: (internat.) +33-5-49454157
E-mail: sylvie.rossignol@univ-poitiers.fr

(OC₃H₇)₃ (ATP) and H₂PtCl₆, with a final treatment at 773 K. They demonstrated that the sol-gel (xerogel) catalyst displays a higher thermal stability of the metal particles than the conventionally impregnated catalyst. For the sol-gel sample, the exposed Pt metal particles are anchored to the alumina surface by metal–oxygen bonding. Other xerogel Pt/Al₂O₃ catalysts prepared by Castillo et al.^[14] and Manasilp et al.^[15] using the same precursors (ATB-ATP, H₂PtCl₆) and treated at 823 K and 773 K, respectively, demonstrate that the co-gelation of alkoxides and noble metals induces the stabilisation of the metallic phase and its incorporation into the alumina network producing better metal-support interactions. Recently, using ATB with acetylacetonate and LiBH₄ as precursors, Sault et al.^[16] demonstrated that after calcination at 873 K, the metal particles are not encapsulated or occluded into the support. All these observations confirm that the metal-support interactions strongly depend on the precursors used, on the thermal treatment and on the method of drying. In order to extend the use of such samples to high temperature applications, it seemed important to study the influence of the drying conditions and to then compare xerogels and aerogels.

In this paper, we present our results on the sol-gel preparation of alumina or alumina doped with silica as a support. A systematic comparison has been made between support samples dried under conventional conditions (xerogels) and under supercritical conditions using CO₂ (aerogels) including the behaviour after the thermal treatment. The introduction of platinum was carried out using the conventional impregnation of dried or calcined sol-gel supports or during the sol-gel process. Powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and thermal analyses (TDA-TGA) were used to determine the structural properties. To determine the effects of the synthesis on the catalytic activity, an evaluation of the properties of the catalyst towards the propellant decomposition has been performed with aqueous solutions of hydroxylammonium nitrate NH₃OH⁺ NO₃⁻ (HAN). The preliminary results are presented here.

Results and Discussion

A. Supports

The diffraction patterns of the four different types of supports, after drying, are presented in Figure 1. They are all composed of nanocrystalline hydrated boehmite γ -AlO(OH)·*n*H₂O, see PDF file 21–1307 mentioned in ref.^[17] The peak positions are essentially identical for all samples which also show the same cell parameters. The shift of the first diffraction peak has been discussed previously.^[18]

The thermal analyses curves (Figure 2) indicate two major weight losses accompanied by endothermic effects which correspond firstly to the dehydration of the hydrated boehmite and then to the transformation of boehmite into gamma alumina. Assuming that at the end of the analyses the final product is the anhydrous α -alumina, the TG curves

enable the determination of evolved water and thus the formula of the initially dried solids. At the beginning of the measurements, the dried samples always contain an excess of water and are known as hydrated boehmites. For both samples presented in Figure 2, the complete formulas are AlOOH·0.94H₂O and (AlOOH)_{0.94}·(SiO₂)_{0.06}·1.0H₂O. Therefore, in the low temperature range (20–800 °C), the behaviour of the doped samples is similar to that of pure boehmites. On the other hand, the TDA curves reveal an important difference at high temperature: the exothermic peak at about 1200 °C which characterises the transformation into alpha alumina is clearly visible in the case of the pure boehmites but is shifted to a higher temperature for the doped samples. In this case, the boehmite is transformed into transition alumina but its structure is more stable and leads to alpha alumina at much higher temperatures (>1350 °C). This thermal behaviour is the same for the aerogel and xerogel samples. Consequently, we expected that the doped samples would not be transformed into alpha alumina, even after a hard thermal treatment (5 h calcination at 1200 °C).

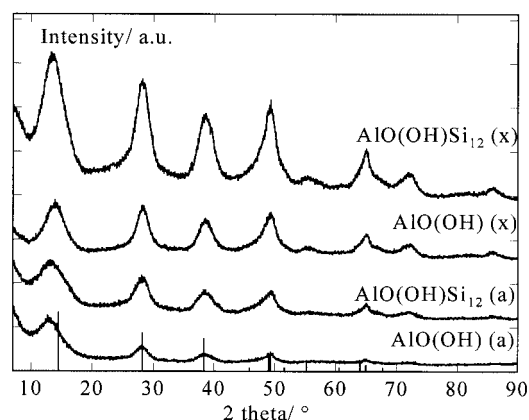


Figure 1. X-ray diffraction patterns of pure and doped boehmites, xerogels and aerogels (lines: PDF file 21–1307).

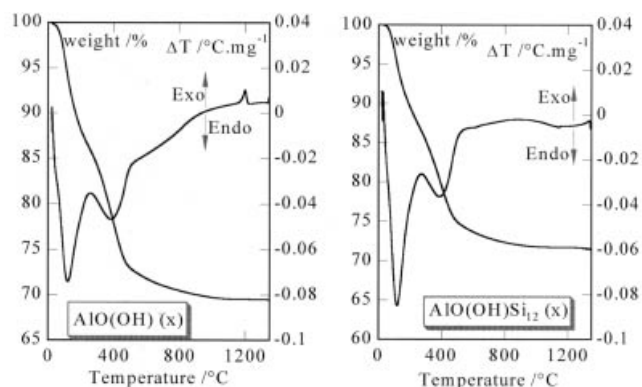


Figure 2. Thermal analyses of dried samples of AlO(OH) (x) and AlO(OH)-Si₁₂ (x)

The diffraction patterns of the calcined supports (Figure 3) confirm this fact, revealing that the transformation into alpha alumina is delayed by doping. After the thermal treatment, the structure of the $\text{Al}_2\text{O}_3\text{Si}_{12}$ xerogel or aerogel corresponds to θ alumina (monoclinic, PDF file 23–1009) with a well ordered structure. By comparison, the non-doped aerogel (Al_2O_3) is entirely transformed into alpha alumina after the same treatment (Figure 7).

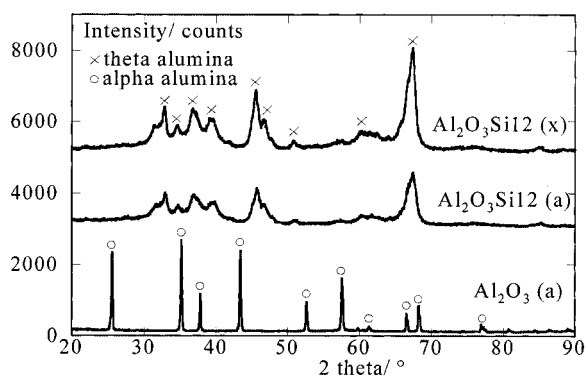


Figure 3. X-ray diffraction patterns of doped samples of $\text{Al}_2\text{O}_3\text{-Si}_{12}$ (a) and (x) and nondoped Al_2O_3 (a), calcined at 1200 °C for 5 h (θ Al_2O_3 , PDF: 23–1009; α Al_2O_3 , PDF: 46–1212)

The values found for the BET surface area of the samples (Table 1) confirm that the doping retards the transformation into alpha alumina. The doped xerogel retains a good specific surface area ($65 \text{ m}^2\cdot\text{g}^{-1}$) whereas the aerogel has a much better value of $120 \text{ m}^2\cdot\text{g}^{-1}$ (compared with $1\text{--}3 \text{ m}^2\cdot\text{g}^{-1}$ for the nondoped alumina). This value is similar to that published by Mizushima,^[8,9] ($114 \text{ m}^2\cdot\text{g}^{-1}$) for a 10% doped sample prepared in an alcoholic medium. The porous volume is slightly larger for the ASi_{12} (a) sample ($0.24 \text{ cm}^3\cdot\text{g}^{-1}$) than for the ASi_{12} (x) sample ($0.16 \text{ cm}^3\cdot\text{g}^{-1}$). The mean pore sizes of the two doped aluminas are comparable at 9.5 and 9.7 nm, respectively.

The transmission electron microscopy images enabled us to analyse the morphology of these calcined supports. Fur-

thermore, the X-ray mapping revealed the atomic distribution of Al and Si across the samples. For the sake of clarity, we present a previously published diagram (Figure 4).^[17] For ASi_{12} (a) (aerogel sample) we can see that the distribution of both aluminium and silicon atoms is homogeneous over the entire zone of the sample which was analysed. Other explored zones show that this homogeneity is a characteristic of the aerogel samples (see 2 in Figure 4). Xerogel sample ASi_{12} (x) contains some zones showing obvious microscale heterogeneity (see 1 Figure 4). This latter sample contains domains where the silicon concentration is enhanced. From EDX analyses, the Si and Al atomic compositions were quantified. For the aerogel, the atomic Si:Al ratio of 6:94 is in excellent agreement with the expected value (6.3:93.7). For the xerogel, this ratio strongly depends on the analysed zone (200 nm). In Figure 4 (1), the analysed zone exhibits a very important excess of silicon: Si:Al = 33:67. In fact, the large (200 nm) dark particle clearly visible on the image of the xerogel (see 2 in Figure 4) contains only silicon and oxygen atoms which correspond to pure amorphous silica. The aluminium content is smaller in the zones where this silicon agglomeration appears. In compensation, other zones are reduced in their silicon content leading to a higher content of aluminium in comparison with the calculated value. In these zones, the aluminium content can reach values as high as 95.7%.

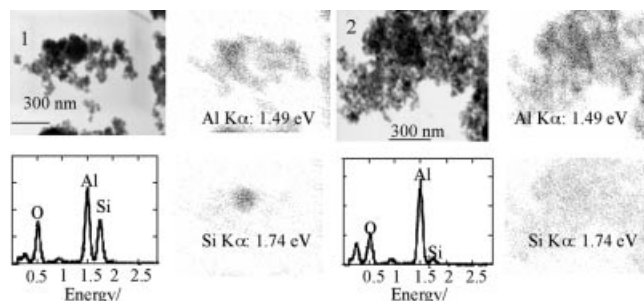


Figure 4. Electron microscopy (X-ray mapping and EDX analyses for the: (1) $\text{Al}_2\text{O}_3\text{-Si}_{12}$ (x) and (2) $\text{Al}_2\text{O}_3\text{Si}_{12}$ (a) samples

Table 1. Samples prepared, mode of platinum introduction, thermal treatment, nomenclature, specific surface area (BET) and experimental platinum load (expected value 5 wt.-%)

Sample	Pt introduction	Nomenclature	BET	Pt	Pt size
aerogel (a); xerogel (x)	impregnation sol-gel		[m ² /g]	[%]	[nm]
Al_2O_3 (a)	1	A (a)	3		
Al_2O_3 (x)	1	A (x)	1		
$(\text{Al}_2\text{O}_3)_{0.88}(\text{SiO})_{0.12}$ (a)	1	ASi_{12} (a)	120		
$(\text{Al}_2\text{O}_3)_{0.88}(\text{SiO})_{0.12}$ (x)	1	ASi_{12} (x)	65		
5% Pt/ Al_2O_3 (a)	SG-1	SG-Pt-B-c (a)	41	3.0	7.0
5% Pt/ Al_2O_3 (x)	SG-1	SG-Pt-B-c (x)	44	3.0 ^[a]	11.0
5% Pt/ $(\text{Al}_2\text{O}_3)_{0.88}(\text{SiO})_{0.12}$ (a)	SG-1	SG-Pt-BSi ₁₂ -c (a)	130	3.5	5.6
5% Pt/ $(\text{Al}_2\text{O}_3)_{0.88}(\text{SiO})_{0.12}$ (x)	SG-1	SG-Pt-BSi ₁₂ -c (x)	41	2.6	4.3
5% Pt/ Al_2O_3 (a)	Imp-2	Pt-A-r (a)	3	2.2 ^[a]	2.6
5% Pt/ Al_2O_3 (x)	Imp-2	Pt-A-r (x)	1	2.6	3.0
5% Pt/ $(\text{Al}_2\text{O}_3)_{0.88}(\text{SiO})_{0.12}$ (a)	Imp-2	Pt-ASi ₁₂ -r (a)	120	2.4	
5% Pt/ $(\text{Al}_2\text{O}_3)_{0.88}(\text{SiO})_{0.12}$ (x)	Imp-2	Pt-ASi ₁₂ -r (x)	68	3.5	3.8

^[a] Values obtained by XRD quantification. 1. calcination at 1200 ° (5 h); 2. reduction at 400 ° (3 h).

The silica segregation can explain the lower specific surface area (Table 1) of the xerogel sample 1-Asil2(x) after the thermal treatment at high temperature. During the transformation of alumina into the alpha form, small sites are first formed by a nucleation process. The corundum formation then continues by a growing and sintering process which requires contact between the former crystallites and migration of cations or cationic vacancies from the alumina particles of the previous transition.^[25]

The stabilising effect of silicon occurs at the surfaces of the crystallites. When the silicon distribution is homogeneous, the silicon atoms are bonded tetrahedrally through μ -oxo bridges $\text{Al}-\text{O}-\text{Si}-\text{O}-\text{Al}-$ and cannot take part at the sintering process because the $\alpha\text{-Al}_2\text{O}_3$ structure contains the cations in octahedral sites. It is much more difficult for these sites to be occupied by silicon. The surface silicon layer behaves as a barrier between the growing areas and limits the transformation. Another explanation for the delay of the transformation into alpha alumina is related to the crystalline structure of the transition alumina. Beyond 600–700 °C, the quantity of surface OH groups contained in alumina is no longer sufficient to maintain the stability of the structure. The removal of these hydroxyl groups leads to the formation of tetrahedral vacancies which destabilise the structure. In the presence of well distributed silicon atoms, the influence of these tetrahedral vacancies is lowered and the transformation is delayed.^[19–22]

The diffraction peaks of the two samples after the high temperature treatment have been enlarged to focus on the peak displacement (Figure 5). We observed a systematic and slight but visible displacement of the aerogel peaks to higher 2θ values. This displacement varies between 0.09 and 0.29° and can be explained by the cell parameters shrinking due to the replacement of aluminium by silicon atoms in the structure. Silicon atoms are slightly smaller than Al atoms (bond length $\text{Si}-\text{O} = 1.91 \text{ \AA}$ compared with $\text{Al}-\text{O} = 2.03 \text{ \AA}$).^[23] If the structure of $\theta\text{-Al}_2\text{O}_3$ can be viewed as a distorted spinel structure,^[24] we can approximate the peak displacement on the basis of a cubic structure. Assuming that all the silicon atoms are located in the tetrahedral sites of the $\theta\text{-Al}_2\text{O}_3$ structure, we can estimate the 2θ displacement from the bond length difference to be of the order of 0.2 to 0.5°. The experimental shifts between the aerogel and the xerogel peak positions range from 0.1 to 0.3°, indicating that the silicon content incorporated into the structure is far superior in the case of the aerogel (of the order of 50%).

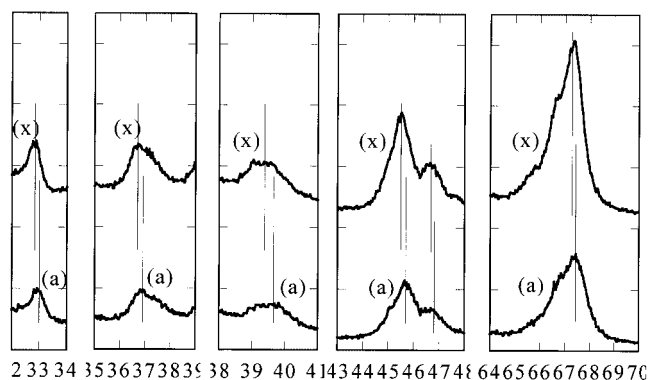


Figure 5. Enlargement of the diffraction patterns of the $\text{Al}_2\text{O}_3\text{Si}_{12}$ samples X: (a) = aerogel, (x) = xerogel

This cell parameter difference does not exist for the non-calcined samples displaying the boehmite pattern (Figure 1). No displacements can be seen, in agreement with the boehmite structure which displays only octahedral aluminium sites. These sites are able to host aluminium atoms but not silicon atoms. During the sol synthesis, boehmite nanocrystallites are formed first by hydrolysis of the aluminium precursor. After addition of the silicon precursor, hydrolysis occurs later and produces silicon species which may be bonded to the surface aluminium atoms of the boehmite particles by a μ_2 -oxo bridge, this being a consequence of an oxolation reaction: $-\text{Si}-\text{OH} + \text{HO}-\text{Al}- \rightarrow -\text{Si}-\text{O}-\text{Al}- + \text{H}_2\text{O}$

Thus, before calcination, silicon atoms are located mainly at the surface of the crystallites and only during the transformation of boehmite into γ alumina can they participate in the transition γ -alumina structure by substituting tetrahedral aluminium atoms. In Figure 6, which shows a possible structural rearrangement during the transformation of boehmite, the surface Si atom is linked to a surface HO group of boehmite and to an external hydroxyl group. The transformation of the hydroxyl group and a slight silicon displacement leads to the position of silica in a tetrahedral site of the transition alumina. The presence of these silicon atoms stabilises the alumina defect structure and can explain the delay in the transformation into corundum.

The results presented in this section show that the drying technique has an important influence on the features of doped alumina. The morphology, thermal stability, homogeneity, fine structure and the textural properties are depen-

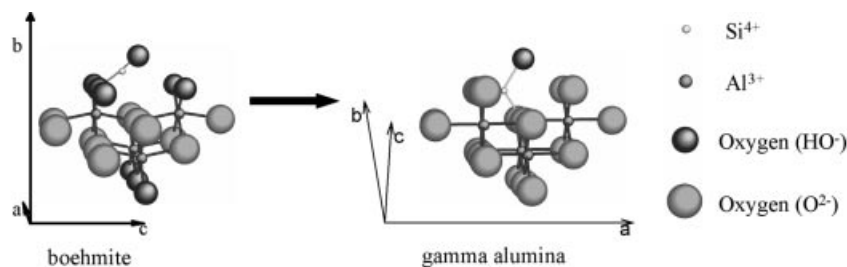


Figure 6. Model of silicon insertion into the gamma alumina structure during the boehmite transformation

dent on this. The ASi12 samples prepared show very interesting porosity values, especially for the aerogel. For this reason, they were chosen as supports for the synthesis of 5 wt.-% platinum on alumina catalysts.

B. Catalysts

1. Effective Catalyst Metal Load

For a selection of catalysts (6 samples), the platinum content was analysed in order to establish precisely the effective metal load after the thermal treatment. For two other samples, SG-Pt-B-c (x) and Pt-A-r (a), the metal load was estimated from a quantitative analysis of the X-ray diffraction patterns with respect to their homologues SG-Pt-B-c (a) and Pt-A-r (x).^[25] The results are presented in Table 1. The metal content is between 47 and 71% of the calculated value, so that a quantity of platinum is lost during the preparation of the catalysts. This loss probably takes place during the thermal treatment processes (calcination and reduction).^[26] During the introduction of the platinum precursor, the anions present in solution ($[\text{PtCl}_6]^{2-}$, $[\text{Pt}(\text{H}_2\text{O})\text{Cl}_5]^-$ or others) are adsorbed into the surfaces of the crystallites and this fixation is mainly due to electrostatic interactions between negative complexes and surface OH_2^+ groups of the support present in acidic solutions or to ligand substitution around the platinum atoms (Cl^- by surface OH groups). The fraction of platinum atoms which is not firmly anchored on the surface can become detached and leave during the thermal treatments, probably in the form of more volatile oxychloride species. Nevertheless, hexachloroplatinic acid remains the best precursor because it allows the preparation of catalysts with high metal dispersions.^[11,27] We expect also a lower metal percentage for the materials displaying the α - Al_2O_3 structure due to the strong decrease of the BET surface area (Table 1).

For the samples supported on doped alumina, this platinum content decrease could be related to the surface Si-OH groups which can prevent the metal from bonding firmly to the surface.^[28]

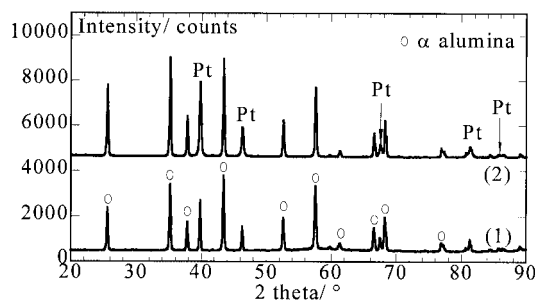


Figure 7. Diffraction patterns of catalysts on nondoped supports: (1) SG Pt-B-c (a) sample; (2) Pt-A-r (a) sample. (PDF: Pt: 04-0802; α - Al_2O_3 : 46-1212)

2. Physico-Chemical Characterisation

a) Catalysts on Nondoped Supports

The diffraction patterns of both aerogel catalysts (sol-gel and impregnated) are presented in Figure 7. As expected, the structure of the support is α - Al_2O_3 and the metal phase appears as large sized crystallites. The average size values calculated from peak breadths are around 70 nm for the sol-gel catalyst and 26 nm for the impregnated one. For the xerogel sample, the respective values are of the same order (Table 1). The sintering is slightly more pronounced for the sol-gel samples compared with the samples prepared by impregnation.

For the Pt-A-r (a) sample, transmission electron microscopy agrees well with this average size. The image reveals a rather large distribution of the crystallite sizes, ranging from a few tenths to several hundred angstroms. We present two different characteristic zones of the sample in Figure 8.

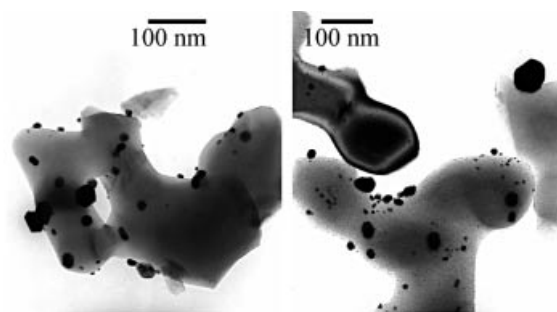


Figure 8. Two transmission electron microscopy images of the Pt-A-r (a) sample

b) Catalysts on Doped Supports

Catalysts Prepared by Sol-Gel Synthesis: The diffraction patterns indicate the presence of θ alumina for the support and the same large metal crystallites (Figure 9) of average size 43 nm for the xerogel and 56 nm for the aerogel. This is the only case when the aerogel crystallites are larger than the xerogel ones. This fact is probably related to the particular texture of the sample of SG Pt-BSi12-c (a). In fact, the precursor anions can be adsorbed onto the boehmite sites concurrently with the silicon species. As a consequent, the

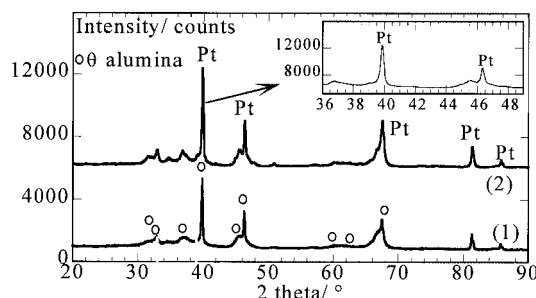


Figure 9. Diffraction patterns of (1) SG Pt-BSi12-c (a) and (2) SG Pt-BSi12-c (x) samples (θ Al_2O_3 , PDF: 23-1009)

surface nature and the interactions between crystallites may be different from the case of a pure boehmite sol.

After the thermal treatment at 1200 °C, the sample SG Pt-BSi12-c (a) exhibits the largest specific surface area ($130 \text{ m}^2 \cdot \text{g}^{-1}$), compared with only $41 \text{ m}^2 \cdot \text{g}^{-1}$ for its xerogel homologue SG Pt-BSi12-c (x). The porous volume is $0.45 \text{ cm}^3 \cdot \text{g}^{-1}$, five times larger than for the xerogel ($0.09 \text{ cm}^3 \cdot \text{g}^{-1}$) and the mean pore sizes are 14 and 7 nm, respectively. Consequently, the platinum crystallites located inside the aerogel pores can develop and reach larger sizes.

The TEM pictures (Figure 10) show, for the xerogel sample, some zones with a normal aspect of the porous support and metal crystallites with sizes ranging from 7 to 100 nm and some other singular zones particles with different textures can be observed. In order to identify the nature of the particles visible on the B image, we recorded three EDX spectra, shown in Figure 11. The first (a) corresponds to a homogeneous zone. We could establish the presence of aluminium and silicon but not platinum. The second reveals platinum crystallites and, finally, the third (c) indicates a large particle containing only aluminium atoms. The appearance of such particles can be explained by the presence of the metal precursor in the boehmite sol in the earlier stages of the synthesis. The competition of adsorption on boehmite crystallites between the platinum and silicon species leads to crystallites covered by more platinum and less silicon. The X-ray analysis reveals that a small fraction of platinum atoms is rather well dispersed over the sample but the other fraction exists as isolated crystallites. In the same way as observed for the supports, some zones with a silicon agglomeration can be identified.

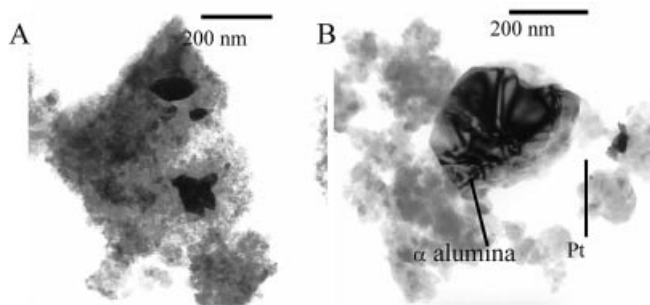


Figure 10. Two transmission electron microscopy images for the sample SG Pt-BSi12-c (x)

For the aerogel, we observed similar behaviour with platinum isolated crystallites and $\alpha\text{-Al}_2\text{O}_3$ particles. The X-ray mapping, performed on a zone around the α alumina par-

ticle, revealed a better silicon repartition compared with the xerogel. Instead, the signal due to the platinum atoms is practically invisible over the zone showing that the metal is present only as isolated crystallites.

Catalysts Prepared by Impregnation on Doped Alumina: The diffraction patterns of the catalysts impregnated on doped alumina are presented in Figure 12. In the case of the aerogel, the peaks corresponding to platinum are practically indiscernible from the background indicating a very small crystallite size. For the xerogel, the platinum peaks are weak but visible. By comparing the intensity of the isolated (311) peak (36 counts degree) with the SG-Pt-BSi12 c (x) sample (which has practically the same metal load, 304 counts degree) we can estimate that only about 10 wt% of the platinum contributes to the diffraction peaks in the Pt-ASi12-r (x) sample. By using the width of the (311) peak, which appears well isolated at $2\theta = 81.3^\circ$, we can estimate a size of 40 nm. In fact, for a large size distribution, the mean value calculated on the basis of peak's width is largely overestimated since the small crystallites make very little contribution and the peak profile is mainly influenced by the large crystallites.^[27,29] We can therefore assume that a large part of the crystallites are small in size and only a small other part of the better developed crystallites will be responsible for the diffraction signal.

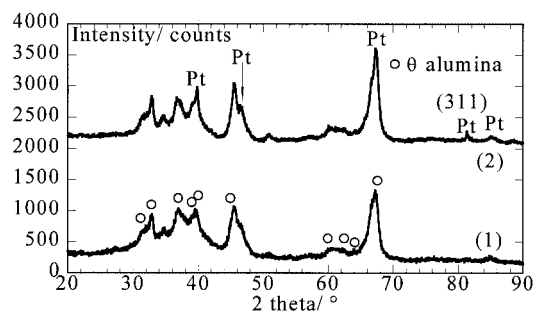


Figure 12. Diffraction patterns of the (1) Pt-ASi12-r (a) and (2) Pt-ASi12-r (x) samples (the circles correspond to $\theta \text{ Al}_2\text{O}_3$, PDF: 23-1009)

The specific surface areas of these catalysts are $68 \text{ m}^2 \cdot \text{g}^{-1}$ for the xerogel and $120 \text{ m}^2 \cdot \text{g}^{-1}$ for the aerogel. This is practically the same as in the supports and indicates no pore blocking which is in agreement with the small sizes of most of the crystallites.

Transmission electron microscopy confirmed these results. For the aerogel, almost all the platinum particles are smaller than 4 nm (Figure 13, left). The xerogel exhibits a

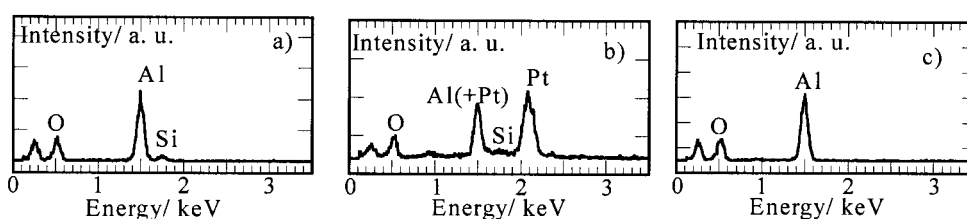


Figure 11. EDX spectra corresponding to different zones of the sample SG Pt-BSi12-c (x)

larger size distribution with crystallites smaller than 4 nm but with larger particles (Figure 13, right). Both histograms are shown in Figure 14 as well as the average crystallite sizes. From the metal dispersion measurements, an average surface crystallite size can be determined (Table 2). Two models may be used, a cubic model with one face in contact with the support and a hemispherical model. The average sizes refer to the cube parameter or the diameter. The results for the aerogel are in good agreement with the average sizes determined from the electron microscopy histogram. For the xerogel, this agreement is poorer because of the larger size distribution revealed by electron microscopy and X-ray diffraction (90% of the platinum appears as crystallites with average sizes of about 4 nm, i.e. 10% larger and visible by XRD). It is also possible that a part of the metal crystallites, located in closed pores, is not accessible for the hydrogen adsorption.^[30,16]

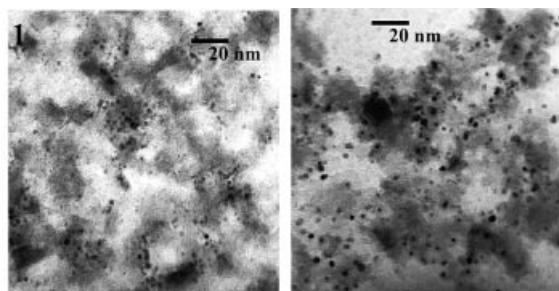


Figure 13. Transmission electron microscopy photos of the (left) Pt-ASi12-r (a) and (right) Pt-ASi12-r (x) samples

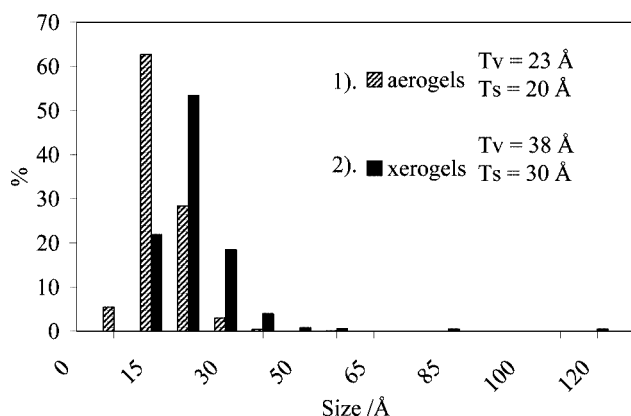


Figure 14. Histogram of the size repartition of the platinum crystallites for the (1) Pt-ASi12-r (a) and (2) Pt-ASi12-r (x) samples (T_v , T_s : see Table 2)

$$T(\text{\AA}) = \frac{K}{D(\%)}$$

$T(\text{\AA})$ = mean crystallite size ($\text{\AA}$) cube: length, hemisphere: diameter

K = constant ($\text{\AA}$) (cube: 946, hemisphere: 568)

Table 2. Comparison between average crystallite sizes determined by transmission electron microscopy or by metal dispersion measurements

Sample	Mean size, microscopy (nm)		Mean size, dispersion (nm)		Dispersion (%)
	T_v	T_s	Cube	Hemisphere	
Pt-ASi12-r (x)	3.8	3.0	6.7	8.2	13
Pt-ASi12-r (a)	2.3	2.0	1.8	2.2	51

$$\bar{T}_s = \frac{\sum_{i=0}^n T_i \cdot S_i}{\sum_{i=0}^n S_i} = \frac{\sum_{i=0}^n T_i^3}{\sum_{i=0}^n T_i^2}$$

$\bar{T}_s$ = surface weighted mean crystallite size ($\text{\AA}$)
 T_i = size of a i particle ($\text{\AA}$)
 S_i = surface of a particle T_i ($\text{\AA}^2$)
 n = number of particles

$$\bar{T}_v = \frac{\sum_{i=0}^n T_i \cdot V_i}{\sum_{i=0}^n V_i} = \frac{\sum_{i=0}^n T_i^4}{\sum_{i=0}^n T_i^3}$$

$\bar{T}_v$ = volume weighted mean crystallite size ($\text{\AA}$)
 T_i = size of a particle i ($\text{\AA}$)
 V_i = volume of a particle T_i ($\text{\AA}^3$)
 n = number of particles

C. Discussion

1. Influence of the Preparation Mode by Impregnation versus the One-Step Method (Sol-Gel)

For the samples prepared by the sol-gel method, the calcination at 1200 °C induces an important sintering of the metal phase, whatever the nature of the support (xerogel or aerogel). The SG Pt-BSi12-c (a) sample is of particular note, displaying a very large specific surface area of 130 $\text{m}^2\cdot\text{g}^{-1}$. This important difference is due to the specific synthetic conditions (simultaneous presence of silicon and platinum species in the sol) as well as to the supercritical drying which allows the retention of the gel morphology. The metal dispersion is not related to the porosity of the support because the mean size of the platinum crystallites for the SG Pt-BSi12-c (a) sample is still greater than 50 nm. Therefore, the metal dispersion is mainly determined by the growth and sintering of the particles.

In contrast, the catalysts prepared by impregnation on calcined alumina contain smaller metal particles because sintering cannot occur during the reduction process. In this case, the dispersion of the metal phase is directly dependent on the specific surface of the support. A large value of the surface area implies a large amount of adsorption centers within the metal precursor (i.e. H_2PtCl_6) and, consequently, the formation of numerous centers for germination of platinum particles during the reduction. The catalysts supported on doped alumina also exhibit special characteristics, especially for the aerogel sample Pt-ASi12-r (a), namely a specific surface area higher than 120 $\text{m}^2\cdot\text{g}^{-1}$ after thermal treatment, good metal dispersion ($> 50\%$) and a homogeneous distribution of silicon and platinum atoms over the sample. As a consequence, this sample could be tested as an interesting catalytic material for applications requiring high temperatures.

Nevertheless, it must be stated that the great difference in dispersion between sol-gel and impregnated catalysts is related to the temperature difference applied to the plati-

num precursor. For the sol-gel samples, the platinum precursor is decomposed to platinum crystallites during the high temperature treatment (1200 °C, 5 h) in an oxidising atmosphere leading to a strong sintering effect. In the other case, the impregnated sample is reduced at low temperatures (see Exp. Sect.) and the maximum temperature experienced by the platinum particles is only 400 °C. To confirm the critical role of the temperature, the xerogel sample (Pt-ASi12-r (x)) was treated with the same high temperature conditions after reduction at 400 °C. A small decrease in the surface area could be observed from 68 m²·g⁻¹ to 43 m²·g⁻¹, accompanied by a strong sintering of the platinum particles. The average size was between 4 nm and 30 nm before treatment and 40 nm after treatment. It must be said that the real catalytic conditions used will not be so drastic, the high temperatures being reached over very short time ranges.

2. Influence of the Drying Mode: Xerogel versus Aerogel

The main advantage of the supercritical drying is the possibility of maintaining the microporosity of the wet gel and obtaining materials with high specific surfaces and porosities. Indeed, the specific surface area of the aerogel supports and catalysts is about 120 m²·g⁻¹ even after a thermal treatment at 1200 °C (5 h). By comparison, the xerogel catalysts reveal a specific surface area respectively for the sol-gel, 41 m²·g⁻¹ and for the impregnated, 68 m²·g⁻¹. Those values are related to the high porosity of the aerogel materials (0.24 cm³·g⁻¹ for the doped alumina and only 0.16 cm³·g⁻¹ for the corresponding xerogel). An other important aspect is the platinum size distribution which is shorter for the catalyst prepared by impregnation on doped aerogel than for the xerogel catalyst. Furthermore, the platinum particles are more homogeneously distributed on the aerogel support. All these remarks display the importance of the drying mode for the final properties of the materials.

D. Catalytic Tests

The decomposition temperatures of the HAN/water mixtures, with and without the presence of supports or catalysts are reported in Figure 15. For the catalysts, the effective

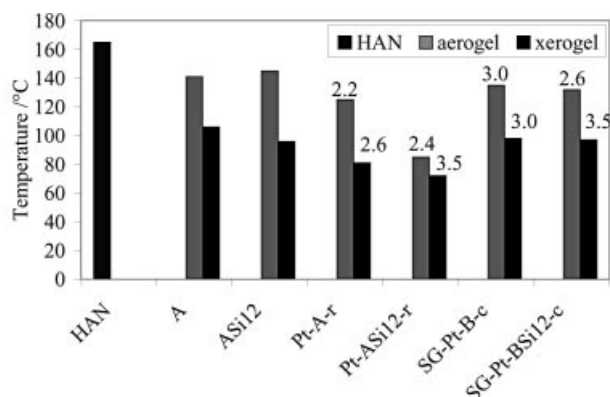


Figure 15. Decomposition temperatures of HAN/water mixtures with and without supports or catalysts and metal content for aerogels and xerogels materials

platinum content is also reported. The decomposition of the HAN_{79%}/water mixture alone appears at a temperature of 165 °C.

All the supports (without the active phase) display a catalytic effect. This effect is more pronounced in the case of the xerogel samples (106 °C for A (x) and 96 °C for ASi12 (x)). For the aerogels, the decomposition temperatures are higher and similar for each sample (140 °C). The very strong difference in the surface area between nondoped and Si-doped alumina seems to have a limited influence on this reaction. The introduction of platinum leads to a further catalytic effect in the case of the impregnated catalysts. A further decrease in the decomposition temperature, in comparison with the support, is of the order of 25 °C except for the Si-doped aerogel which display a decrease of 60 °C. For the sol-gel catalysts, the effect of platinum is much more limited.

With regard to the supports, the effect of the surface area remains very limited for the catalysts except for the impregnated aerogel samples Pt-ASi12-r (x) which display an important decomposition temperature decrease (from 125 °C to 85 °C) related to the surface area increase (1 m²·g⁻¹ to 68 m²·g⁻¹). For both samples the platinum is of the same order. The higher decomposition temperatures of the sol-gel catalysts compared with the impregnated catalysts are mainly due to the platinum particles sintering during the calcinations leading to a very low platinum accessibility. This effect is clearly observed for the samples Pt-ASi12-r (x) and SG-Pt-BSi12-c (x) which have the same effective metal content (3.5%) but exhibit a decomposition temperature difference of 20 °C. This indicates the importance of the preparation mode.

The comparison between aerogel and xerogel supports and catalysts shows that the xerogel samples are always more efficient (Figure 15). A possible explanation for this difference can be related to the higher insulation properties of the aerogels.^[31] Due to its lower thermal conductivity and higher porosity, the temperature within the aerogel is lower than the measured crucible temperature, leading to a temperature difference higher than for xerogels and thus to a higher measured decomposition temperature. Moreover, when the exothermic decomposition starts on the external surface of the catalyst powder, the release energy propagates more slowly to the centre of the aerogel powder resulting in a delay in the decomposition reaction of the monopropellant.

Catalysts supported on silicon-doped alumina are promising for high temperature applications. Moreover, xerogel catalysts have been revealed to be better than aerogel catalysts despite the heterogeneous dispersion of silicon. To confirm this hypothesis, studies must be carried out on the decomposition characteristics, i.e. the temperature increase, pressure increase and ignition delay.

Conclusion

We have synthesised sol-gel materials based on pure or doped alumina using classical and supercritical drying con-

ditions. For the supports, the morphology, thermal stability, homogeneity and the structure depend strongly on the drying technique used. The ASi12 sample displays a high porosity and it was selected as support of catalyst.

A general characteristic of all catalysts is that a fraction of the platinum is lost during the preparation of the catalysts and the real metal content is between 47 and 71% of the calculated value (5 wt.-%).

The comparison between the aerogel and xerogel samples displays, respectively, a fine distribution on the surface and a heterogeneous distribution of the metallic phase. This feature can be linked to the larger specific surface area of the aerogels.

The introduction mode of platinum by impregnation leads to smaller particles which are well dispersed. On the other hand, the sol-gel method results in the formation of large particles.

Finally, from our evaluation experiments on HAN solutions, the best catalytic activity is displayed by platinum catalysts prepared by impregnation on Si-doped xerogel alumina.

Experimental Section

A. Preparations

a) Support: Pure Alumina and Doped Alumina

The preparation procedure for pure alumina and Si-doped alumina $[(\text{Al}_2\text{O}_3)_{0.88}(\text{SiO}_2)_{0.12}]$ by the sol gel method has been described in previous work and is shown in Figure 16.^[6] The ASi12 label for this material (Table 1) indicates the final molar composition (after drying and firing) as $\text{SiO}_2/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.12$. The silica weight percent in the dried sample is 7.4%, corresponding to an atomic ratio Si:Al = 6.3:93.7.

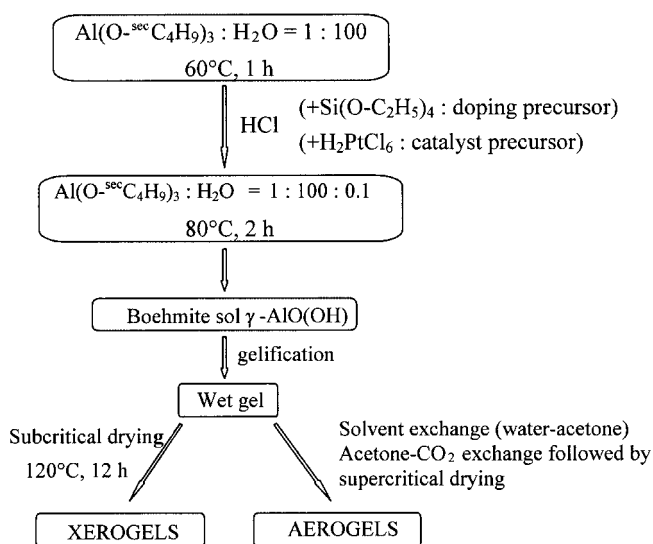


Figure 16. Scheme of the sol-gel preparation procedure

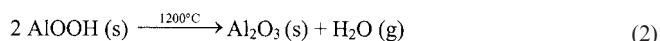
To prepare 2 g of support, aluminium tri-*sec*-butoxide (8.48 g, 0.0334 mol, 97%, Aldrich) and pure water (60.1 g, 3.34 mol) were

stirred at 60 °C for 1 h. Concentrated hydrochloric acid (0.28 mL, $3.3 \cdot 10^{-3}$ mol, $12 \text{ mol} \cdot \text{L}^{-1}$) and, if necessary, tetraethoxysilane (0.51 mL, $2.24 \cdot 10^{-3}$ mol, 98%, Aldrich) as a doping precursor were then added and the temperature was raised and maintained at 80 °C for 2 h.

The xerogel samples were obtained after drying overnight at 120 °C in a ventilated oven. For the aerogel samples, about 75% of the water content evaporated at 80 °C over 3 h affording a viscous sol which was poured in the drying mould (stainless steel, $d = 3.6 \text{ cm}$, $h = 3.5 \text{ cm}$). A 5-mm hole in the bottom of the mould enables the solvent exchange. After 15 h, the solvent exchange started: water was replaced first by acetone (complete miscibility) and then acetone was replaced by CO_2 just before the supercritical drying. The solvent exchange procedure was as follows: the wet gel was covered with acetone (about 25 mL) and the solvent was evacuated through the bottom hole before the addition of acetone (25 mL, three times a day over 5 days). The mould was then introduced into the autoclave (300 mL, Parr Instruments) and acetone (100 mL) was added. The autoclave was equipped with two entries (liquid CO_2 and argon) and two outflows (gas and liquid) and the temperature and the pressure can be controlled as shown in Figure 17.

The reactor was filled with liquid carbon dioxide using several filling and purging steps in order to quantitatively evacuate the acetone and the air contained in the autoclave. Upon completely filling the autoclave with liquid CO_2 , a temperature difference was obtained between the bottle (room temperature) and the autoclave (water cooling system). The temperature difference (about 4–5 °C) was sufficient to push liquid CO_2 into the reactor because the pressure in the bottle (55 bar at 20 °C) exceeded the equilibrium pressure in the reactor (49 bar at 14 °C). After complete filling, the pressure was about 55 bar (Figure 18, point 1). The reactor was isolated and the temperature increased from 15 °C to 40 °C which led to an important pressure increase (step 1–2) up to 140–150 bar (inside the supercritical domain). After 1 h, the supercritical fluid was evacuated over 1 h at the same temperature and the pressure was decreased to 1 bar (step 2–3). The heating was then turned off and argon was flushed through the reactor (step 3–4). The aerogel was then taken out of the reactor.

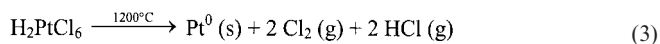
Pure boehmites and Si-doped boehmites (aerogels and xerogels) were calcined at 1200 °C under air for 5 h (ramp of $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$) to obtain pure or doped aluminas.



b) Supported Platinum Catalysts (5 wt.-%)

The catalysts were prepared by two procedures: (i) a one step procedure using the sol-gel method or (ii) an impregnation procedure on a calcined support (pure or doped alumina).

Sol-Gel Procedure: The platinum precursor solution (H_2PtCl_6) was introduced during the preparation of the support in the sol with the hydrochloric acid (see Figure 16). The preparation procedure follows the same steps used for the support (drying, calcination at 1200 °C). The high temperature calcination induces the formation of metal by a redox reaction:^[1]



Impregnation Procedure: A volume of the metallic solution (H_2PtCl_6) corresponding to the porous volume of the support

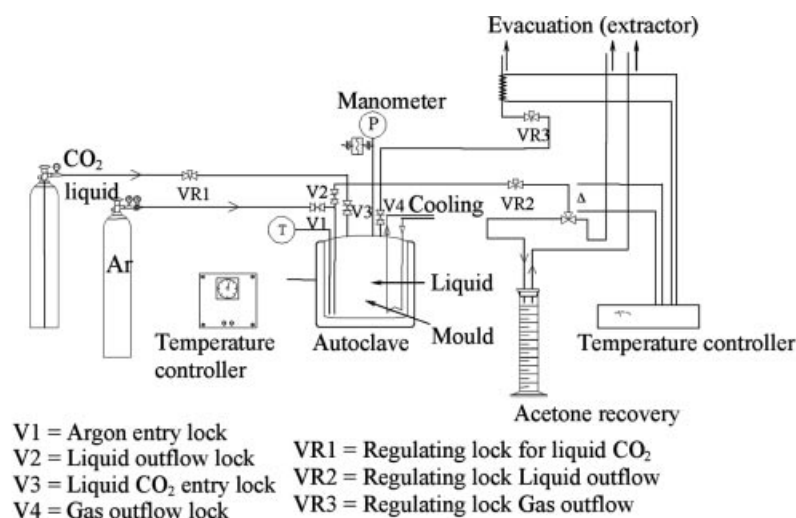


Figure 17. Diagram of the supercritical drying apparatus

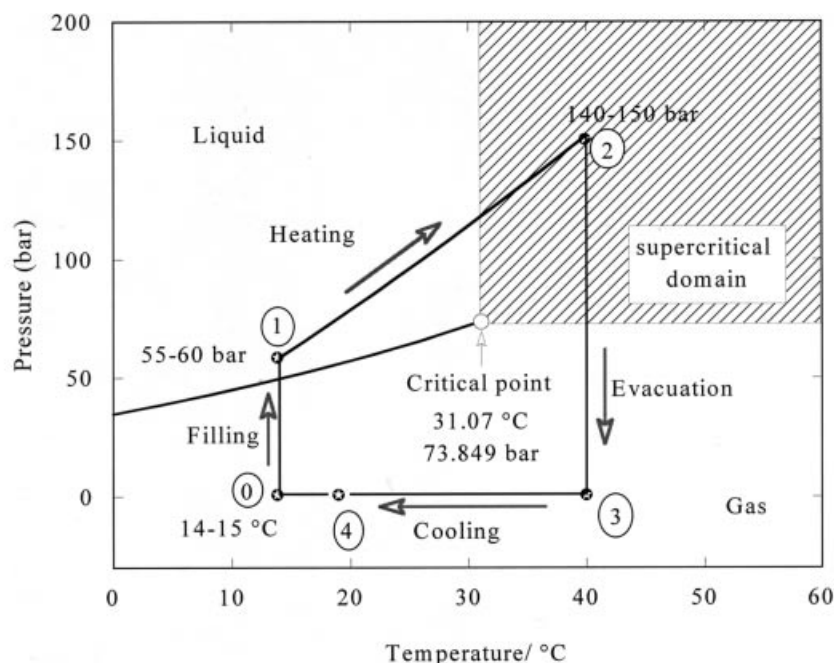
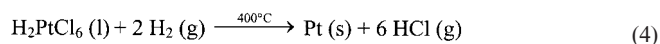


Figure 18. Diagram of the pressure and temperature for supercritical drying

(1.5 mL·g⁻¹) was added to the alumina (wetness impregnation). The concentration of the solution was then calculated giving a metal content of 5 wt.-%. The catalysts were dried overnight at 120 °C, calcined at 400 °C for 3 h under air (20 mL·min⁻¹) and reduced under H₂ (20 mL·min⁻¹) for 1 h at 200 °C and 2 h at 400 °C to obtain platinum supported alumina.



Whatever the procedure, the introduction of the metallic precursor did not affect the acidity (pH near 1).

B. Characterisations

The effective metal load was determined from the CNRS analyses. The specific surface areas of the samples were determined by the BET method from the nitrogen adsorption isotherms at -196 °C in an automated Micromeritics ASAP 2000 apparatus after evacuation for 1 h 30 min at 350 °C. The method used is a simple BET 7 points procedure with P/P_0 values between 0.05 and 0.25. The complete adsorption and desorption isotherm was obtained for a few samples leading to the porous volume values.

Differential thermal analyses (DTA) and thermogravimetric analyses (TGA) were recorded in order to characterise the supports after

drying. TDA-TGA experiments were carried out between 25 and 1350 °C using a thermal analyst 2100 TA instrument with platinum crucibles. The samples were heated in a nitrogen flow (100 mL·min⁻¹) with a ramp of 10 °C·min⁻¹.

Diffraction patterns and particles sizes were determined by X-ray diffraction (XRD) experiments performed on a Siemens D 5005 powder θ - θ diffractometer using the Cu- $K\alpha$ radiation ($\lambda_{K\alpha} = 0.15186$ nm) and a graphite monochromator. The diffraction patterns were obtained under the following conditions: dwell time: 2 s, step: 0.04°, constant divergence slit: 1°.

Crystalline phases were identified by comparison with PDF standards (Powder Diffraction Files) from ICDD. (AlOOH: 21-1307, α -Al₂O₃: 46-1212, θ -Al₂O₃: 23-1009, Pt: 04-0802)

The average crystallite sizes (D) were determined from the Scherrer equation: $D = (0.9\lambda)/(B\cos\theta)$, $\lambda = 0.15186$ nm, B is the width at half maximum and θ the Bragg angle for the peak in question (rad). For boehmite, the peak (020) was used without any correction due to the very small size of the particles. For platinum, the peaks (311) and (222) were used and a width correction was introduced, i.e. $B_{\text{cor}} = (B_{\text{exp}}^2 - B_{\text{inst}}^2)^{1/2}$. To determine B_{inst} , the analysis of standard LaB₆ powder was performed under the same conditions. The widths of the peaks were obtained by profile analyses using a pseudo-voigt function from the diffract AT software (socabim, France).

The structural pictures were obtained using the software CaRine Crystallography.^[32]

The platinum dispersion was obtained by hydrogen chemisorption at room temperature with a lab-build apparatus using pressure measurements. The samples (300 to 500 mg) were reduced at 400 °C over 1 h under a static pressure of hydrogen, degassed at this temperature over 1 h and cooled to ambient temperature. The adsorption isotherms enabled the determination of reversibly and irreversibly adsorbed hydrogen. The dispersion was calculated using the stoichiometric ratio H/Pt = 1.^[4]

Platinum particle sizes and size distributions were obtained from transmission electron microscopy using a Philips CM 120 microscope with a linear resolution of 3.5 Å. Analyses by EDX enabled us to determine the distribution and quantification of atomic species (Al, Si and Pt). The lines used were $L\alpha$ at 9.441 keV (Pt), $K\alpha$ at 1.486 keV (Al) and $K\alpha$ at 1.739 keV (Si), respectively.

C. Catalytic Tests

All samples were tested by the decomposition of an aqueous solution of HAN (hydroxylammonium nitrate, 79 wt.-%) prepared by water evaporation of a 20 wt.-% HAN solution [from SME (SME: French society of explosive materials)] in a rotating evaporator apparatus at 50 °C under vacuum conditions (water pump), the concentration was controlled by density measurements. The experiments were carried out in a TDA-TGA apparatus which gives a good estimation of the decomposition temperature.^[4] The procedure was as follows. After placing the sample (15 mg) in an aluminium pan with a cover, the propellant was added with a micropipette (10 μ L). The system was heated (10 °C·min⁻¹) to 250 °C under an argon flow (100 cm³·min⁻¹). An example of the catalytic decomposition is given in Figure 19. The inflexion point of the temperature curve indicates the decomposition temperature. The analyses by TDA-TGA allowed us to obtain the following information: (i) the onset temperature of the decomposition, (ii) the concentration of the HAN solution at decomposition and (iii) the efficiency of the catalyst, i.e. the exothermic peak. The weight loss after a completed reaction is often different from the expected value

due to the high exothermicity of the decomposition which destroys a small amount of catalyst.

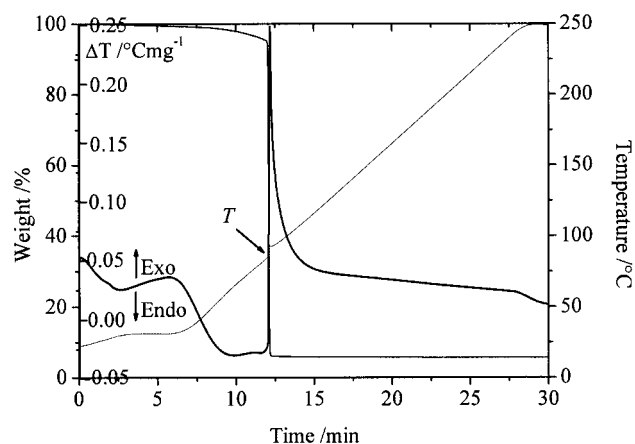


Figure 19. Example of the catalytic decomposition temperature of a HAN/water mixture on Pt-Asi-r (x)

Acknowledgments

The authors thank all the people working in the “service de Mesure Physique” of the LACCO.

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Received July 28, 2004

Early View Article

Published Online December 6, 2004