Characterization of alumina surfaces by fluorescence spectroscopy. Part 1. Grafting a pyrene derivative on γ- and δ-alumina supports

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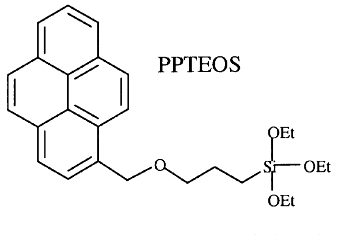
Received (in Strasbourg, France) 5th October 2001, Accepted 28th November 2001
First published as an Advance Article on the web 15th March 2002

With the aim of characterizing the proximity and the distribution of hydroxyl groups on alumina surfaces by fluorescence spectroscopy, a fluorophore containing a pyrene moiety linked to a triethoxysilane group (PPTEOS) was synthesized and grafted on the surface of two alumina supports (γ-Al_2O_3 and δ-Al_2O_3) at different surface concentrations. Elemental analysis showed that the grafting of PPTEOS was less efficient on the δ-Al_2O_3 as compared to the γ-Al_2O_3. This observation is in full agreement with IR spectroscopy measurements on the commercially available γ-Al_2O_3 and δ-Al_2O_3 dehydrated at 823 K. Information on alumina sintering can thus be obtained. The ability of pyrene to form excimers was used to detect probes that were in close proximity to each other and thus gave indirect information of the distribution of hydroxyl groups on the surface. The fluorescence intensities and surface concentration data indicated that pyrene derivatives chemically bound to alumina were not homogeneously distributed but rather clustered in regions. A scheme of the distribution of hydroxyl groups on the alumina surface is proposed.

Aluminas have been used in a number of heterogeneous catalytic reactions, serving both as catalytic supports[1] and as catalysts in their own right. They have found applications from petroleum refining[2] to automotive emission control.[3] Characterization of the surface properties is important with the aim of understanding the catalytic properties. The nature of the alumina surface has been extensively studied by infrared spectroscopy[4,5] and NMR.[6] Much of the work to date has focussed on the determination of the total surface density of hydroxyl groups and their acido-basic properties. But there has been almost no investigations on the proximity and the distribution of hydroxyl groups on alumina surfaces. This aspect has been already studied for silica surfaces by using a chlorosilane derivative of pyrene grafted to microparticulate silica.[7–12] The capability of pyrene to form excimers can then be used to detect probes that are in close proximity. An inhomogeneous distribution of chemically reactive silanols has been found on these surfaces.[5]

The aim of this work is to graft a pyrene group on γ- and δ-alumina surfaces, to compare the reactivity of those two aluminas towards grafting and to study the fluorescence emission in order to determine the distribution and the proximity of chemically accessible hydroxyl groups on alumina surfaces. These aluminas come from the same crystalline boehmite precursor but they have different transition phases: a low-temperature transition phase for γ-Al_2O_3 and a high-temperature transition phase for δ-Al_2O_3.[13] The structural differences between the two families are relatively small as all transition aluminas belong to the cubic system. Differences are much more important for the surface reactivity aspect.

For the grafting on silica surfaces, Lochmüller and Kersey[8] used a pyrene derivative bearing a chlorosilane group: 3-(3-pyrenyl)propylmethyl chlorosilane (3PPS). This derivative was very sensitive to moisture, the purification by distillation at 200 °C under vacuum was very difficult and characterization by NMR spectroscopy was not possible. The amount of fluorescent probe introduced was thus difficult to estimate. On the other hand, the grafting of an ethoxysilane group on an alumina surface has been already described by Sarrazin *et al.*[14] Thus, we have chosen, as a fluorophore, a pyrene derivative containing a triethoxysilane group PPTEOS.



PPTEOS

In the present paper, the synthesis of this derivative and its grafting on alumina surfaces are described. Fluorescence emission spectra of the grafted alumina are reported.

DOI: 10.1039/b109144c

Experimental

General procedures

^1H and ^{13}C NMR spectra were recorded at room temperature on a Brüker AC 400 spectrometer; chemical shifts are reported in ppm with protonate solvent as internal reference ($^1H : CHCl_3$ in $CDCl_3$ $\delta = 7.26$). Elemental analyses were performed at the Institut de Chimie des Substances Naturelles (France). Toluene and DMF obtained from SDS were distillated prior to use.

Synthesis

1-Allyloxymethylpyrene. 1. Pyrenemethanol (4.0 g, 17.2 mmol) was added to a solution of sodium hydride (60% in mineral oil, 895 mg, 22.4 mmol) in DMF (100 ml). The solution was stirred for 1 h at room temperature. After addition of allylbromide (1.7 ml, 19.6 mmol) under argon atmosphere and stirring for 24 h at room temperature, ethanol (10 ml) was carefully added to eliminate the residual NaH. The mixture was evaporated *in vacuo*. After addition of water (100 ml), the product was extracted with EtOAc (300 ml). The organic solution was dried over $MgSO_4$ and evaporated *in vacuo*. Column chromatography (SiO_2, cyclohexane–EtOAc 90:10) gave **1** (1.9 g, 7.0 mmol) as an oil with 41% yield. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.17$ (dt, $J^3 = 5.69$ Hz, $J^4 = 1.40$ Hz, 1H, OCH_2CHCH_2), 5.25 (s, 2H, $ArCH_2$), 5.26 (ddt, $J^3 = 10.37$ Hz, $J^2 = 1.68$ Hz, $J^4 = 1.25$ Hz, 1H, $OCH_2CHCH^{cis}H^{trans}$), 5.38 (qd, $J^3 = 17.25$ Hz, $J^{2,4} = 1.65$ Hz, 1H, $OCH_2CHCH^{cis}H^{trans}$), 6.05 (ddt, $J^3 = 17.22$ Hz, $J^3 = 10.36$ Hz, $J^3 = 5.68$ Hz, 1H, OCH_2CHCH_2), 8.02 (m, 4H, ArH), 8.17 (m, 4H, ArH), 8.37 (d, $J = 9.26$ Hz, 1H, ArH); anal. calcd for $C_{20}H_{16}O$: C, 88.2; H, 5.92; found C , 88.47; H, 5.98.

[3-(Pyren-1-ylmethoxy)propyl]triethoxysilane 2. 1 (450 mg, 1.65 mmol) was suspended in dry toluene (10 ml). Hexachloroplatinic acid (0.1 M solution in isopropanol, 34 µl, 3.40 µmol) was added to the solution under argon atmosphere. After stirring for 1 h at room temperature and addition of triethoxysilane (95%, 365 µl, 1.88 mmol), the mixture was heated at reflux for 4 h. The solution was evaporated *in vacuo*. The crude product was purified by column chromatography (SiO_2, cyclohexane–EtOAc 90:10) to give **2** (350 mg, 0.80 mmol) as an oil with 49% yield. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.69$ (t, $J^3 = 8.31$ Hz, 2H, $SiCH_2$), 1.20 (t, $J^3 = 7.03$ Hz, 9H, OCH_2CH_3), 1.79 (q, $J^3 = 6$–7 Hz, 2H, $SiCH_2CH_2$), 3.61 (t, $J^3 = 6.78$ Hz, 2H, $SiCH_2CH_2CH_2$), 3.79 (q, $J^3 = 7.00$ Hz, 6H, OCH_2CH_3), 5.23 (s, 2H, $ArCH_2$), 8.02 (m, 4H, ArH), 8.16 (m, 4H, ArH), 8.39 (d, $J = 9.26$ Hz, 1H, ArH); anal. calcd for $C_{26}H_{32}O_4Si$: C, 71.52; H, 7.39; found: C, 71.44; H, 7.42.

Sample preparation and characterization

Alumina γ_c-Al_2O_3 (Puralox SCFa-$\underline{\gamma}$) and δ-Al_2O_3 (Puralox SCFa-$\underline{\delta}$) were obtained from Condea Chemie. Those two samples were obtained starting from crystalline boehmite of Pural type. The γ_c-Al_2O_3 was obtained by phase transition of crystalline boehmite at 923 K. The γ_c-Al_2O_3 alumina particles with 32 µm mean diameter are made of small platelet-like crystallites.[15] The N_2 BET surface area of γ_c-Al_2O_3 is 235 m^2 g^{-1}. The pore size distribution exhibits a broad peak centered at 6 nm. The δ-Al_2O_3 was obtained by phase transition of crystalline boehmite at 1150 K. The 48 µm mean diameter particles are made of large agglomerates. The N_2 surface BET is 104 m^2 g^{-1}. The pore size distribution exhibits a narrow peak centered at 12 nm. These aluminas were activated at 823 K for 3 h under helium prior to use (temperature ramp speed 10 °C min^{-1}). Following thermal activation, the samples were allowed to cool to room temperature under argon. Surface area and pore volume determinations have been obtained with an automatic sorptometer Micrometrics (ASAP2405Kr) using the BET equation. The physical characteristics of the studied aluminas are shown in Table 1.

Table 1 Specific properties of γ- and δ-alumina

	γ	δ
Surface area/m^2 g^{-1}	235	104
Pore diameter (top)/nm	6 ± 2	12 ± 3
Pore diameter (bottom)/nm	8 ± 3	17 ± 7

Grafting of 2 on alumina particles

Grafting of PPTEOS on alumina supports (γ- and δ-Al_2O_3) was done at two different concentrations per unit surface (respectively 0.27 and 0.53 molecule nm^{-2}) to give γ-1, δ-1, γ-2 and δ-2. A suspension of alumina particles (1.2 g) in dry toluene (20 ml) was stirred for 30 min under argon atmosphere. A solution of an appropriate amount of [3-(pyren-1-ylmethoxy)propyl]-triethoxysilane, PPTEOS, in dichloromethane (3 ml) was slowly added dropwise through a pressure-equalizing dropping funnel to the mixture. The reaction mixture was stirred at room temperature for 1.5 h and was heated at reflux for 20 h. Grafted alumina particles were centrifuged (5×10^3 rpm) with chloroform (120 ml) and methanol (160 ml) and dried at 50 °C for 2 days.

The amounts of grafted pyrene were measured by atomic emission of silicon at the IFP and by elemental analyses of the carbon at the Institut de Chimie des Substances Naturelles (France).

Spectroscopic measurements

Acetonitrile from Aldrich (spectrometric grade) was used as a solvent for spectroscopic measurements.

Corrected emission spectra were obtained on a Spex Fluorolog 1681 spectrofluorometer. Fluorescence measurements were done in a 1 cm quartz cuvette containing a magnetically stirred suspension of grafted alumina (1 mg) in 2.5 ml of solvent. The emission spectra were obtained after stirring the suspension of grafted alumina for 6 h (for details see ref. 16).

Fourier transform infrared spectra (FTIR) were recorded at room temperature with a Nexus Apparatus after pretreatment, typically at 450 °C overnight under secondary vaccum to completely eliminate residual water present in the sample. The sample was pressed into a self-supporting disk 16 mm in diameter weighing 20 mg and held with a stainless steel sample holder. The IR spectra were recorded with a 4 cm^{-1} resolution.

Results and discussion

Characterization of the alumina samples

Before grafting, the commercially available γ- and δ-aluminas were dehydrated at 823 K. Thus, the amount of hydroxyl groups on the surface was estimated to be 3 OH nm^{-2} according to the work of Vitt *et al.*[17] A preliminary study of the support was carried out by IR spectroscopy in order to compare the different hydroxyl groups present on the surface. Fig. 1 displays the IR spectra of γ- and δ-alumina (vacuum activated at 450 °C) in the 3500–3900 cm^{-1} region. The observed spectra are composed of three main bands respectively at ~3690, ~3730 and ~3800 cm^{-1}, which were previously

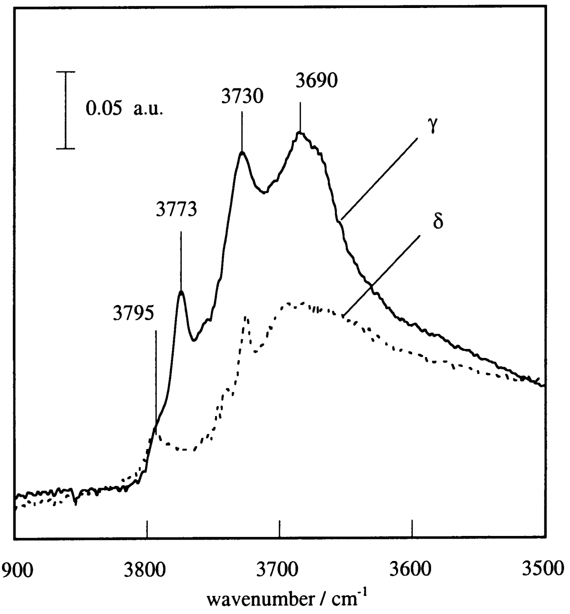


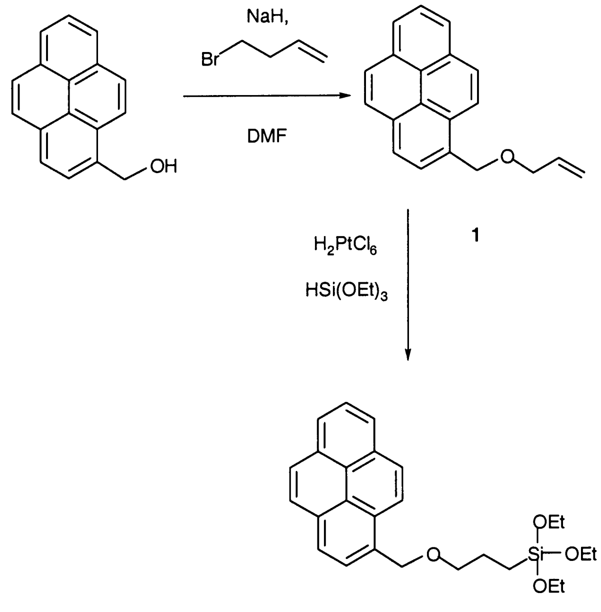
Fig. 1 IR spectra of δ-alumina and γ-alumina in the ν_{OH} region.

assigned to surface hydroxyl groups by Tsyganenko and Filimonov.[18] According to the basicity scale for hydroxyl groups on an alumina surface proposed by Knözinger and Ratnasamy,[2] the acidic hydroxyl groups give a band at 3695 cm^{-1}, the neutral groups are present at 3730 cm^{-1} and the highest wavenumber band corresponds to the most basic hydroxyl groups (~3800 and ~3780 cm^{-1}). The band at ~3780 cm^{-1} is assigned to terminal hydroxyls I_a on tetrahedral Al^{IV}. The 3800 cm^{-1} band is characteristic of hydroxyl bonds to octahedral aluminum (Al^{IV}). Morterra and Magnacca[15] have attributed the band at 3775 cm^{-1} to Al^{IV} that are present in large amounts in crystallographic defects such as ridges and corners. Fig. 1 shows that for all bands, δ-alumina contains lower amounts of hydroxyl groups on the surface compared to γ-alumina, which is consistent with the high crystalline order reported for δ-Al_2O_3.[19] But in particular, the disappearance of the band at 3773 cm^{-1} and the enhancement of the band at 3795 cm^{-1} were observed for γ-alumina compared to δ-alumina. This effect was already observed for similar compounds by Morterra *et al.*[20]

Synthesis and grafting of the pyrene probe

A pyrene derivative having a triethoxysilane group was synthesized according to the procedure shown in Scheme 1. Pyrene methanol was alkylated with allyl bromide to obtain **1**. Silylation of compound **1** with triethoxysilane in the presence of H_2PtCl_6 afforded PPTEOS, **2**. ^1H and ^{13}C NMR and elemental analysis confirmed the structure of the related compounds.

The grafting of PPTEOS on alumina, considering that the ethoxysilane group of the pyrene derivative reacts with the surface hydroxyl groups of Al_2O_3,[21] was achieved by refluxing a suspension of alumina in a solution of PPTEOS in toluene according to the procedure described by Sarrazin *et al.*[14] For each alumina (γ and δ), grafting was carried out at two different concentrations per unit surface. The amount of pyrene introduced was chosen to be 0.27 and 0.53 molecule nm^{-2}, respectively, which led to samples γ-1, γ-2 for γ-Al_2O_3 and δ-1, δ-2 for δ-Al_2O_3. The surface coverage was measured by elemental analysis of carbon and the measurements were validated by analysis of the silicon for the sample γ-1. The analytical data of the obtained grafted alumina are reported in Table 2. For δ-1, the amount of grafted pyrene is lower than the detection limit, thus the amount of grafted pyrene is estimated to be lower than 0.06 molecules nm^{-2}.



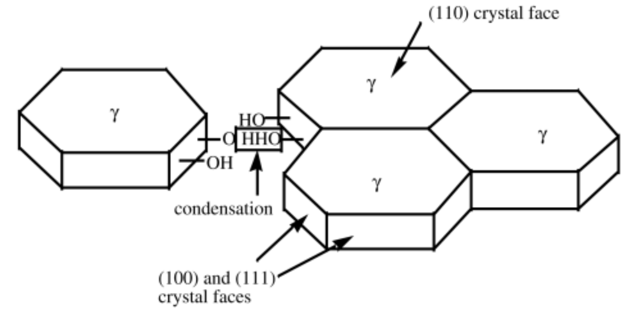
Scheme 1 Synthesis of PPTEOS.

Table 2 Analytical data of PPTEOS modified alumina and steady-state excimer/monomer I_E/I_M ratio as a function of surface coverage or average distance D_a

Sample	Introduced amount of PPTEOS/ molecule nm^{-2}	Surface coverage/ molecule nm^{-2}	D_a/Å	I_E/I_M[a]
γ-1	0.26	0.10 ± 0.03	34 ± 5.5	2.5
γ-2	0.53	0.23 ± 0.03	21 ± 1.4	7.2
δ-1	0.28	<0.06	>47	3.6
δ-2	0.52	0.07 ± 0.03	40 ± 8.8	7.0

[a] Ratio of the areas under the monomer and the excimer fluorescence bands

In all cases, the surface coverage was lower than 0.3 molecule nm^{-2}, assuming a monolayer dispersion of the pyrene on the surface. For each alumina, the amounts of grafted pyrene probes follows the amounts introduced, which were two times larger for samples −2 than for samples −1. Nevertheless, a large difference in the reactivity of PPTEOS towards grafting on γ- and δ-aluminas was found. An average of 40% of the introduced PPTEOS was grafted on γ-alumina. In the case of δ-alumina only about 10% of the introduced PPTEOS was grafted on the surface. This can be explained by a difference in reactivity of the hydroxyl groups on alumina surfaces. Sarrazin *et al.*[22] showed that tetraethoxysilane (TEOS), which has a similar reactivity as PPTEOS, reacts preferentially with the more basic hydroxyl groups (at 3775 cm^{-1} in the IR spectrum), and does not react with the neutral or the acidic hydroxyl groups of γ-alumina. Morterra and Magnacca[15] reported that the very high reactivity of the OH groups (located at 3775 cm^{-1}) was in good agreement with their high accessibility to reacting molecules. These hydroxyl groups are located in particularly exposed areas such as structural defects (corner, ridge or step) and are present in large amounts for γ-alumina. In the case of δ-alumina, the basic hydroxyl groups at 3774 cm^{-1} are nearly absent. Thus, the reactivity difference toward grafting is in full agreement with the IR spectroscopy



Scheme 2 Proposed scheme for sintering of γ-alumina → δ-alumina.

measurements and the known difference in surface reactivity for these alumina; indeed, δ-alumina is known to be less active than γ-alumina.[15]

These results are in accordance with the alumina sintering mechanism proposed by Euzen.[23] The reactive hydroxyl groups, which are present in large quantity for γ-alumina disappear in the case of δ-alumina. The sintering to obtain δ-alumina results from aggregation of crystallites of γ-alumina and involves the condensation of the hydroxyl groups at 3775 cm^{-1}. Scheme 2 summarizes the proposed mechanism for the sintering process.

Characterization of the packing

The surface concentration (molecule nm^{-2}) of bonded pyrene was calculated by the method described by Unger[24] from both carbon analysis and specific surface area. The average distance between two neighboring bonded pyrene probes (Å) was calculated from the surface concentration according to the same procedure as used by Unger[24] and by considering the pore diameter.

Molecular modeling using MM^+ as the force field was used to estimate the minimum and the maximum distances between PPTEOS bonding sites that would allow excimer formation. Fig. 2 presents the two extreme structural conformations in which excimer formation is possible; they are called fully extended (a) and collapsed (b) conformations, respectively. For both conformations, the average interchromophoric distance between the pyrene rings was found to be 3.4 Å, which is in agreement with the distance previously reported.[25] The obtained distances between PPTEOS bonding site structures for fully extended and collapsed pyrene probes are respectively 4.6 and 19 Å. The distance in the case of collapsed pyrene is close to that estimated by Lochmüller *et al.*, to be 18.4 Å in the case of 3PPS bonded on silica surface.[9] We can thus predict that excimer formation is possible if the distance between two bonding sites ranges from 4.6 to 19 Å.

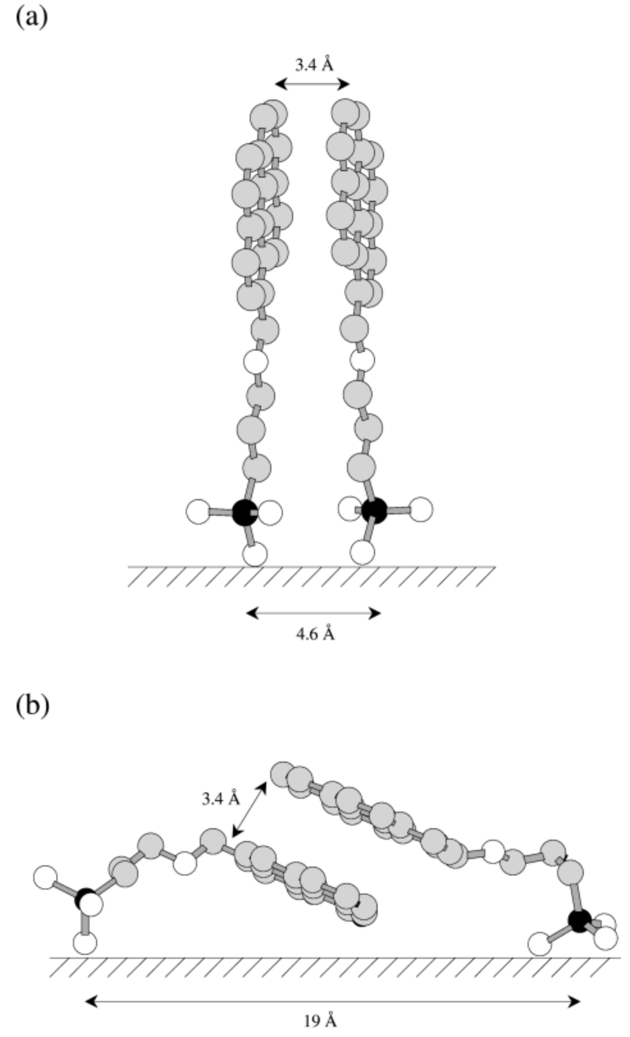


Fig. 2 Energy-minimized structures of grafted PPTEOS generated with MM^+ using Hyperchem 4.5 (Cambridge Software): (a) fully extended and (b) collapsed configurations.

Fluorescence spectra

Fig. 3 displays the emission spectra of grafted aluminas recorded in the presence of acetonitrile. In all cases, they consist of a structured band around 390 nm characteristic of the emission of pyrene monomers and a broad band around 480 nm that is ascribed to excimer emission. The ratios of the intensities of fluorescence emitted by excimers and monomers are given in Table 2.

As expected, the yield of excimer emission for γ- and δ-alumina increases with pyrene loading concentration (*cf.* sample-1 to sample-2). For all samples, the average distance between two pyrene probes calculated on the basis of surface concentration is larger than the maximum distance for excimer formation as estimated by molecular modeling (see above). This provides evidence that there are some regions where the

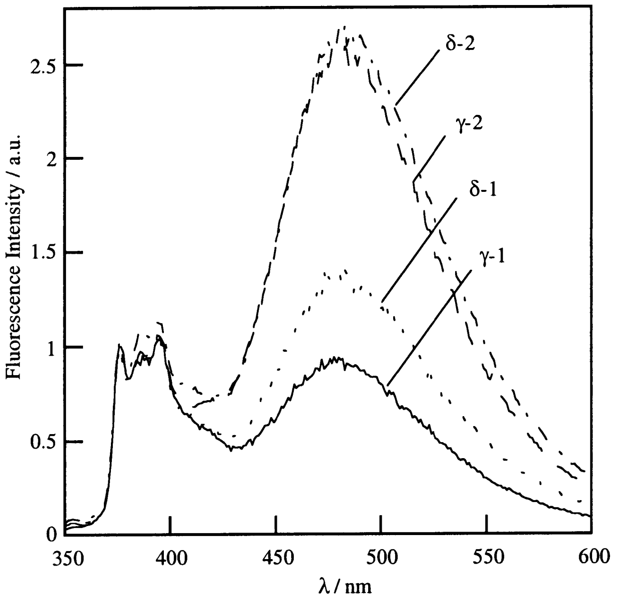


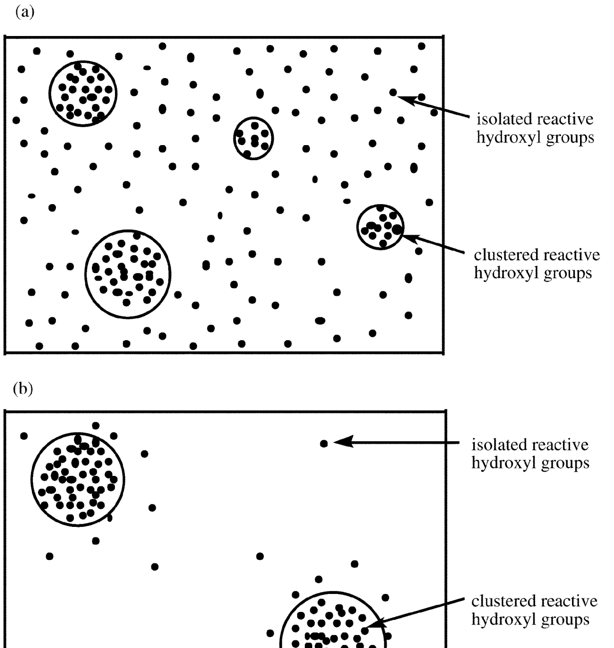
Fig. 3 Corrected emission spectra of grafted alumina in suspension in acetonitrile. (1 mg per 2.5 ml of solvent) normalized to the monomer peak at 390 nm. Excitation wavelength is 315 nm.

distance between bound pyrene silyl groups is small enough for excimer formation. Thus, the molecules are not homogeneously distributed but are rather clustered within regions of high density.

The comparison of the distributions of reactive hydroxyl groups on the γ-alumina and the δ-alumina is possible by means of the fluorescence spectra provided that the samples contain an equivalent amount of pyrene probe per unit surface. This is the case of the samples γ-1 and δ-2 for which the amount of pyrene probe on the surface is close to 0.1 molecule nm^{-2}. The ratio of the intensities of fluorescence emitted by excimers and monomers, I_E/I_M, was found to be 2.8 times larger for δ-alumina than for γ-alumina, which means that the pyrene probes are more clustered on δ-alumina than on γ-alumina. A similar reasoning applies to the comparison of the samples δ-1 and γ-1. The sample δ-1 contains less pyrene probes on the surface as compared to alumina γ-1 but the ratio I_E/I_M is 1.4 larger for the δ-alumina.

A tentative schematic plane representation of the distribution of the reactive hydroxyl groups on the γ-alumina and δ-alumina is shown in Scheme 3. According to the IR measurements and the grafting experiments the total amount of reactive hydroxyl groups is smaller on δ-alumina as compared to γ-alumina. Both alumina surfaces consist of clustered regions of reactive hydroxyl groups (in which the distances between these groups are smaller than 19 Å so that excimers can be formed) surrounded by a region in which the reactive hydroxyl groups are isolated (*i.e.*, the distance between bonded pyrene probes is higher than 19 Å and excimer formation is impossible). For δ-alumina, the amount of reactive hydroxyl groups in high density zones is larger than for γ-alumina, which can be explained by the sintering process and the disappearance of zones with a low density of hydroxyls. This is in full agreement with the observations of Liu and Truit during calcination.[26]

It is important to note that the present investigation using excimer formation from bonded pyrene probes provides information on the relative amount of clustered and isolated reactive hydroxyl groups, but not on the size of the clustered zones.



Scheme 3 Tentative plane schematic representation of the distribution of reactive hydroxyl groups on (a) γ-alumina and (b) δ-alumina.

Conclusion

Grafting of the PPTEOS probe on two different microcrystalline phase transition aluminas (γ-Al_2O_3 and δ-Al_2O_3) offers a method to study the reactivity difference of the hydroxyl groups on the surface. The difference in reactivity of these alumina supports is in good agreement with the IR spectroscopy studies. In addition, the emission spectra show that there are some regions in which the reactive hydroxyl groups are clustered and the relative quantity of those groups was shown to depend on the type of alumina. In the case of δ-alumina, the reactive hydroxyl groups are more clustered as compared to the γ-alumina, which can be explained by the diappearance of zones with low hydroxyl density during the sintering process.

Further information on the surface and in particular on the distribution of reactive hydroxyl groups can be provided by time-resolved fluorescence experiments. The results will be published in the second paper of this series.[16]

Acknowledgements

The authors would like to thank Christelle Legens and Nadine Bücher from the French Petroleum Institute for the development of the analytical method to quantify the amount of silicon of grafted alumina.

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