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Hydrophobisation of mesoporous γ-Al₂O₃ with organochlorosilanes – efficiency and structure

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Abstract

γ-Al$_2$O$_3$ materials with small mesopores are hydrophobised by reactions with organochlorosilanes in liquid media. The structure of the modified materials is studied by means of physisorption and high-resolution SEM. A good measure of the decrease in surface polarity can be obtained from BET-fits of the N$_2$ isotherms. It was found that many pores become blocked by using chlorosilanes with bulky organic groups, while a more open structure is preserved for methylchlorosilanes. Using toluene as a solvent leads to a higher extent of modification than ethanol, as observed for methylchlorosilanes. Multifunctional organochlorosilanes (i.e. with 2 or 3 Cl-groups) are more reactive but also give rise to blockage of some of the microporous part as a result of polymerisation reactions. Mono- and difunctional methylchlorosilanes give the best results for alumina materials with small mesopores, preserving an open structure and leading to homogeneous modification. Modification with methylchlorosilanes in toluene leads to the lowest surface polarity. The results

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1

give clues for optimising the procedures for hydrophobisation of porous materials with small mesopores.

Keywords: Mesoporous γ-alumina; Grafting; Silylation; Hydrophilic/hydrophobic modification; Pore blockage

1. Introduction

Porous alumina is employed as an adsorbent for a range of applications, including chromatography, heterogeneous catalysis and membrane technology. Characteristics that contribute to its applicability include chemical as well as a high mechanical and thermal stability. Alumina is frequently used as a catalyst carrier, as its high strength makes it resistant to erosion, guaranteeing a long catalyst lifetime. Moreover, the surface can be made either acidic or basic by simple treatments. The highly porous γ-alumina phase has the largest range of applications of the aluminas, and is commonly used for hydrotreating, hydrocracking, hydrogenation, reforming and methanation. In membranes, $\gamma\text{-Al}_2\text{O}_3$ can be used either as an intermediate layer between an α-alumina support and a selective microporous top-layer or as a selective mesoporous layer on a support [1-3]. As the surface is typically occupied by a large number of hydroxyl groups, enabling strong H-bonding with water, $\gamma\text{-Al}_2\text{O}_3$ is hydrophilic by nature. Whereas crystalline microporous silicas such as silicalite are hydrophobic due to their specific structure, amorphous SiO_2 is also highly hydrophilic [4,5]. Employment of microporous and mesoporous amorphous silica and alumina in wet atmospheres will thus lead to rapid filling of the pores, which impairs the applicability in moist gas mixtures. Under severe conditions, hydrothermal stability becomes an important factor, as water may 'dissolve' M-O-M bonds (M=Al,Si), which

2

will eventually give rise to another physical structure. In the case of membranes and chromatography, this leads to destruction of the separation functionality and thus limits the operating conditions under which they can be applied.

Adsorption of water can be inhibited if surface hydroxyl groups are replaced by hydrolytically stable groups with a hydrophobic character, such as alkyl or phenyl. For silica, one approach is to build in this organic functionality by in situ hydrolysis and condensation of alkoxide precursors with hydrophobic side groups, such as organosilanes or bridged silsesquioxanes [6]. By this method, de Vos et al. were able to prepare hydrophobic silica layers using a combination of tetraethoxysilane and methyltriethoxysilane as the hydrophobisation agent, which resulted in a microporous silica membrane with methyl groups incorporated in the silica structure [7]. However, as such hybrid precursors do not exist for alumina, the most obvious approach for mesoporous materials is post-modification by grafting the internal pore surface with hydrophobic groups. One of these possible hydrophobisation methods is a chemical reaction between chloride groups of an organochlorosilane with the surface hydroxyl groups. A thermally stable chemically bound layer is thus formed, which imparts the desired hydrophobicity. Agents with long organic tails have a significant effect [8], as only one bond with the solid material is needed for the creation of a large hydrophobic surface, shielding several OH-groups at a time. However, application of these reagents may be limited for materials with small pore sizes due to steric hindrance. Multifunctional organosilanes, i.e. with two or more reactive groups, may undergo more extensive coupling with the OH-groups, and may thus especially reduce the number of vicinal OH-groups that are responsible for the strongest hydrophilic interaction [4,5,9]. However, they may also react with each other, thereby forming a polymeric layer with only a small number of covalent bonds to the surface, which can however be quite effective in surface hydrophobisation [10,11]. Various reports exist on successful modification of unsupported materials such as used for

3

chromatography [12-15] and of composite materials such as membranes, e.g. by fluorinated silanes [16-18], chloro- and alkoxyorganosilanes [19-20]. For catalyst preparation, a large number of post-modification procedures with various functional groups have been studied, e.g. [21]. In selected systems, catalyst activity can be enhanced by hydrophobisation of the surface [22,23]. Few studies, however, exist on preservation of the structure [24,25], especially for alumina. Nevertheless, structural preservation is an important additional requirement if separation applications are considered, which is even more so the case for materials with small mesopores.

Infra-red (IR) characterisation of membranes showed that the extent of grafting depends on the nature of the silanes used and was achieved most effectively with multifunctional agents. The N_2 adsorption and desorption isotherms showed a decrease in surface area and micropore volume for membranes silylated with $Me_2Si(OEt)_2$ or $MeSi(OEt)_3$, indicating that the pore wall had been covered by grafted moieties [26]. Van Gestel [8] reported the effect of surface modification of γ-Al_2O_3/TiO_2 multilayer membranes with difunctional (2 chloride groups) C1 and C8 silanes for applications involving non-polar organic solvents. The highest hydrophobicity for mesoporous membranes was obtained with C8 silanes, which supports the view that silanes with long organic tails are advantageous. For microporous membranes, the authors concluded that silane coupling reactions took place in pores situated at the outer membrane surface, while reactions at the internal surface were sterically hindered for both C1 and C8 silanes.

In a previous study [11], we investigated the modification of γ-alumina membranes with various organochlorosilanes by means of XPS and DRIFTS and reported the permeability of the membranes towards both polar and nonpolar liquids. In order to enhance understanding of the observed effects, we now study the structural changes

4

induced by modification of the unsupported materials, which can be characterised well by sorption techniques. γ-Al_2O_3 was used with a pore size of about 4 nm. In concordance with ref. [11], we applied a series of monofunctional, difunctional and trifunctional organochlorosilanes with organic groups of different sizes, in order to assess the influence of functionality and size of the silane on the extent of grafting and on the structure. Easily applicable liquid phase silination with the addition of a nucleophile (water) was chosen for its high reactivity at low temperatures [24]. Several procedures were followed to study the effect of the solvent and of H_2O addition. Surface and pore modification were studied by N_2 and CO_2 physisorption, TPO-MS, and SEM.

2. Experimental

2.1. Materials preparation

Mesoporous γ-alumina flakes were prepared from a boehmite sol, which was dried and subsequently calcined at 873 K in air, as described in detail in ref. [27]. Chlorotriphenylsilane ($(C_6H_5)_3SiCl$, CTPhS, 96% purity), *tert*-butylchlorodimethylsilane ($(CH_3)_3CSi(CH_3)_2Cl$, tBCDMS, 97% purity), chlorotrimethylsilane ($(CH_3)_3SiCl$, CTMS, 99% purity), dichlorodimethylsilane ($(CH_3)_2SiCl_2$, DCDMS, 99% purity) and trichloromethylsilane ($(CH_3)SiCl_3$, TCMS, 97% purity) were all obtained from Aldrich. The γ-alumina materials were hydrophobised by immersing them for a period of 12 h (unless stated otherwise) in 2-5 wt.% solutions of the above-mentioned precursors. An average 4 g of material was prepared at a time. The procedures are summarised in table 1. In all cases, an excess of silane was present in order to enable full hydrophobisation of the Al_2O_3

5

surface, i.e. reactions could take place with all OH-groups in the material. As the reaction rates of the precursors under different conditions vary, some differences in preparation time were followed. The chlorosilanes with large organic groups (tBCDMS, CTPhS) and the multifunctional TCMS are more soluble in toluene than in water or alcohols. These precursors were allowed to react with the alumina surface in toluene with 5 vol% water (samples A2, A4 and A8). The systems were refluxed at 323 K in order to enhance dissolution of the precursors. A8 was refluxed for just 2.5 h due to the comparatively high reactivity of TCMS. Alternatively, tBCDMS and CTPhS were dissolved in pure toluene - without water - and the reaction was carried out at room temperature for 24 h (A1 and A3). CTMS and DCDMS were dissolved in ethanol with 5 vol% water at room temperature (A6 and A7), while the influence of the solvent on modification by CTMS was further studied by dissolving this agent in toluene with 5 vol% water, again at 323 K (A5). After removal from the solution, the alumina flakes were rinsed 5 times with ethanol and dried at 473 K for 1 h in a flow of N_2 (100 ml/min, purity 99.999%) with heating/cooling rates of 0.5 K/min.

2.2. Materials characterisation

Thermogravimetric Analysis-Mass Spectrometry was carried out in a Setaram TG 85 thermobalance. The weight was recorded as a function of temperature during heating in synthetic air (20% O_2 in N_2, 99.999% purity, 60 ml/min). Initial masses were typically 150 mg. Heating was carried out at 10 K/min from room temperature to 1073 K (held for 30 min). A correction for the temperature-dependency of the buoyancy was performed. Analysis of reaction products was simultaneously carried out by means of a quadrupole mass spectrometer. In this way, carbon-containing molecules and fragments could be identified in the off-gas, which assisted in estimating the extent of surface modification.

6

Adsorption/desorption isotherms of N_2 (77 K) and CO_2 (273 K) were determined on a CE-Instruments 1990. All materials were pre-treated by evacuation below 10^{-4} mbar at 473 K. Continuous corrections were being made for variations in the atmospheric pressure p_0. Surface areas and *C*-values were determined by BET-3 fits [28,29] of N_2 adsorption isotherms between $p/p_0 = 0$ and 0.5, according to:

$$n/n_m = C(p/p_0)/(1 - p/p_0) \times (1 - (N+1)(p/p_0)^N + N(p/p_0)^{N+1}) /$$

$$(1 + (C-1)(p/p_0) - C(p/p_0)^{N+1}) \qquad (1)$$

with *n* the gas adsorbed at relative pressure p/p_0, n_m the monolayer capacity of the surface, both in mol per g adsorbent, *C* a constant related to heat of adsorption and thus to the adsorbate-adsorbent interaction and *N* the number of adsorbed layers. From the 3-parameter fits of the isotherms (eq. 1), surface areas *A* were determined with:

$$A = n_m a_m N_A \qquad (2)$$

in which a_m is the area occupied by a N_2 molecule in the completed monolayer, assumed to be 0.162 nm^2, and N_A Avogadro's number.

Mesopore size distributions were obtained from BJH fits [30] of the N_2 desorption isotherms between $p/p_0 = 0.35$ and 0.9. This method is based on Kelvin's equation, stating that condensation occurs in pores with radius r_K at a relative pressure p/p_0, which for cylindrical pores is represented by:

$$\ln(p/p_0) = -2 \gamma_s V_{mol} / RTr_K \qquad (3)$$

with γ_s the surface tension of the liquid-vapour interface (8.85 mJ/m^2 for N_2), V_{mol} the molar volume of the condensed N_2 (34.7 cm^3), *R* the gas constant and *T* the temperature. During desorption, as the relative vapour pressure decreases, the larger pores are opened first. The t-layer remains after all pores are opened, and

7

desorbs subsequently. For a cylindrical pore, the relation between the real pore radius (r_p) and the Kelvin radius (r_K) is

$$r_p = r_K + t \qquad (4)$$

where t is the thickness of the t-layer formed on the inner surface of the pores. We used values that are dependent on the interaction between adsorbate and adsorbent (i.e. on C) as determined by Lecloux [31].

Total pore volumes were determined at $p/p_0 = 0.95$. In order to allow comparison of the different samples, the adsorbed amounts are expressed in terms of the volume of the adsorbed N_2 liquid, with a density of 0.8086 g/cm^3.

Surface areas from CO_2 adsorption isotherms were determined from fits according to the Dubinin method, modified by Kaganer [32,29], between $p/p_0 = 7\times10^{-4}$ and 1.2×10^{-2}, represented by:

$$\log n = \log n_m - D (\log p_0/p)^2 \qquad (5)$$

with D an adsorbate-dependent constant. The surface area can subsequently be calculated according to eq. (2), assuming the area a_m occupied by a CO_2 molecule is 0.179 nm^2.

High resolution Scanning Electron Microscopy was carried out on a LEO Gemini 1550 FEG-SEM at a voltage of 2.0 kV.

3. Results and Discussion

3.1. Extent of modification

8

By heating in synthetic air, a weight loss was observed by TGA-MS for all materials. The weight loss is due to desorption of physisorbed water and dehydroxylation on one hand and to oxidation and decomposition of organic groups on the other. The latter contribution could be observed from the MS signals of CO_2 and other organic components, and evidences that modification of the alumina surface with silanes was successful. However, both the weight loss as observed by TGA and the release of organic species – including CO_2 – as observed by MS took place over a broad temperature range. As a consequence, it was not possible to distinguish between the contributions of dehydroxylation and that of desorption and oxidation of organic fragments by means of the MS response. However, by considering the weight losses above 473 K (the pre-treatment temperature for N_2 physisorption), and comparing these to the weight loss of as-calcined unmodified γ-alumina, a good impression of the total extent of modification could be obtained such that the various modification procedures can be compared. These data are expressed in percentages of the end mass (i.e. after calcination in air at 1073 K) in table 2. Clearly, the weight loss for calcined – unmodified – γ-alumina is small, and no organic components were detected. Modification with the bulky tBCDMS and TCPhS and also with CTMS/toluene has led to a roughly similar amount of organic groups in the alumina. Moreover, the rate of oxidation was at a maximum around the same – high – temperature, i.e. 720 K, so it can be assumed that the organic surface structures were tightly bound. Thermal analysis of methylethoxysilanes by Alami Younssi showed a maximum at similar temperatures [26]. The smaller extent determined for TCMS can be associated with the short preparation time (2.5 h as compared to at least 12 h for the other silanes) which has deliberately been held in view of the high reactivity of TCMS [11]. The extent of modification with DCDMS and CTMS in EtOH was much more limited. The bonds between the silanes and γ-Al_2O_3 were earlier found to be stable towards water exposure [11], which was evident from an

9

unchanged silane concentration present on the surface as observed by DRIFT Spectroscopy.

3.2. Physical structure

Adsorption/desorption isotherms were determined for both pure and silinated γ-alumina. N_2 isotherms are shown in Figure 1 and the corresponding analytical data are given in table 2. The isotherms of unmodified γ-Al_2O_3 and the methylsilane-grafted materials indicate monolayer-multilayer adsorption [33]. The steep desorption branches correspond to a type IV b for samples A and A6-A8, with some percolation effects. This is typically associated with materials with narrow necks and a relatively low level of pore connectivity. The isotherm of sample A5 is more of the type II b, which is typical for aggregated plate-like particles with non-rigid slit-shaped pores, suggesting some change in the pore structure. Samples A1-A4 exhibited much more limited capillary condensation, and the isotherms even tend towards the microporous type I b. All pore volumes were smaller after grafting with silanes, notably of the tBCDMS and CTPhS-modified materials (A1-A4). Grafting with methylsilanes in ethanol only had a limited effect on the pore volume (A6-A7), but a toluene environment led to a more extensive decrease for CTMS (A5) and TCMS (A8). This is also in line with the larger amounts of organic species found in these materials.

For CTPhS in pure toluene (A3), equilibrium could not be reached within a reasonable period (i.e. within 1-2 h) during N_2 physisorption, which results in entirely non-overlapping adsorption and desorption branches. The low N_2 surface area determined is also related to the extremely slow adsorption process. Adsorption of CO_2 (table 2), on the other hand, gives a surface area in the same order as those of

10

the other samples, although the precise values differ with a (constant) factor with respect to those obtained with N_2 adsorption, which is most likely related to differences in the mechanism of micropore filling. For CO_2 adsorption, equilibrium is reached more quickly, which can well be explained by the higher temperature during adsorption. As the organic chains are far less rigid at 273 K than at 77 K, this will enable easier passage of the gas molecules towards the inner pores. Remarkably, the extent of modification of this sample is about equal to that of a sample modified at 323 K in an environment with water added (A4), which does not exhibit such extensive pore blockage. We may thus conclude that pore blockage was determined by the distribution of the silanes, which may be different under other conditions, rather than by the extent of modification. For the materials prepared at room temperature without water, the silanes did not dissolve entirely into the liquid. Moreover, the water that was pre-adsorbed on the surface instead of separately added water may have acted as a nucleophile. As a more direct reaction between the Cl-groups and OH suffers from more steric hindrance than one between two OH groups, this would make reactions in the inner pores even less probable. These differences may have had an effect on the final distribution of the silanes on the surface, such that blockage of the pores occurred, impairing passage of N_2 molecules at 77 K.

The N_2 surface areas of the other modified materials are just somewhat smaller after modification, and vary only slightly. Clearly, the decrease in pore volume is not necessarily accompanied with a smaller surface area. This is an indication that the pore size distribution has decreased to smaller values. Assuming cylindrical pores, the mean pore size can be estimated with the relation:

$$d_p = 4 \, v_p \, / \, A \tag{6}$$

with d_p the pore diameter, v_p the pore volume and A the surface area. A relation can thus be perceived between the extent of modification (corrected for the mass loss

11

observed for sample A) and the decrease of the mean pore diameter, as shown in Figure 2. Figure 3 shows that there is a roughly linear relation between the pore volume and the mean pore diameter, which indicates that the changes in surface area are small indeed. The odd point is related to sample A3, for which no reliable isotherm could be obtained. Two different trendlines can be distinguished, one related to samples A, A5, A6 and A7 and the other related to samples A1, A2, A4 and A8. In order to be more comparable to the first series (the original material and the DCDMS and CTMS-modified samples), the latter one should have smaller pore diameters than have been calculated now. If globular pores are assumed, the relation is $d_p = 3 \, v_p \, / \, A$, resulting in smaller mean pore diameters with the same values for v_p and S. It is thus expected that for these samples the shape of the pores has become more globular with respect to the original γ-Al_2O_3. In practice, this means that inhomogeneous modification or pore-clogging took place, which was clearly most extensive for A3. Although less clearly observable, a similar difference between these series can be noticed in figure 2. For the first series (open symbols), extrapolation of the data would give a zero average pore diameter at about 71 wt% modification, for the second one (closed symbols), this would be around 45 wt%. The larger effect of modification on the mean pore diameter for the second series is another indication of more extensive pore plugging and thus of inhomogeneous modification.

For alumina modified with bulky silanes, capillary condensation was strongly suppressed, indicating significant loss of mesopores (larger than 2 nm). In addition, the lower amounts adsorbed at low p/p_0 indicate loss of the volume of the microporous part of the pore distribution. Mean mesopore sizes were determined, as far as they could be assessed, from BJH fits of the N_2 desorption isotherms (table 2), assuming no percolation effects. The mean mesopore diameters are in line with the trend in the total pore volumes and consequently with the estimated mean pore

12

diameter. No mesoporosity could be observed for sample A3 as no equilibrium had been reached. Grafting with both DCDMS and CTMS in ethanol hardly led to loss of mesoporosity. We may conclude that these agents give rise to a very homogeneous decrease of the pore size, which has also been found earlier for difunctional methylsilanes in mesoporous solids [8]. More extensive loss of mesoporosity is found for CTMS and TCMS in toluene. For CTMS, even another isotherm type is found, indicating slit-shaped non-rigid pores. This may be associated with strong modification of the pores with (flexible) organic groups, although without leading to extensive pore clogging. Modification with TCMS led to a bimodal mesopore size distribution, corresponding to a decrease of the number of pores with sizes around 5 nm, and, more obviously, to loss of microporosity (again visible from the lower amount adsorbed at low p/p_0). As the size of TCMS is about the same as that of CTMS, extensive polymerisation is the most likely explanation for both differences. This results on one hand in selective mesopore modification (mostly of the larger pores) and, on the other, in blockage of the passage of N_2 molecules at 77 K towards part of the micropores. From XPS measurements on membranes treated in similar ways, this was already postulated [11], and the current results give further substantiation. It was also found before that the bulky silanes were mainly deposited on the outer surface. Both structural effects have been confirmed here as these treatments led to inhomogeneous modification.

For all methylsilanes, steric hindrance is limited, so these reactants can enter into the pores most easily during grafting. It is expected that especially CTMS leads to direct and homogeneous modification of the alumina surface, as only direct attachments to the surface can be formed, and no polymeric networks as for DCDMS and TCMS. However, modification also seemed to be quite homogeneous for DCDMS. In a future study, the structural effects of modification with dimethyl and trimethyl

13

chlorosilanes will be compared more systematically for porous materials with a range of pore sizes.

With SEM, clear differences were found between the unmodified and modified γ-Al_2O_3 materials. For the original unmodified alumina, porosity was visible with pore sizes below 10 nm, as well as irregular structures on a scale of about 100 nm, including structures with a fibrous morphology (Figure 4a). This sample suffered from excessive contrast, though. For the slightly CTMS-modified sample A6 (Figure 4b), contrast of the large structures was moderate, and as a consequence the small mesopores and the fibrous structures were more clearly visible. The material that was most 'closed' to adsorption, i.e. sample A3, merely displayed a hazy image (Figure 4c), under which the surface structure was poorly resolved. Moreover, the sample suffered from severe charging, which is another indication of strong surface modification.

3.3. Hydrophobicity and surface polarity

After silination, all materials were calcined in N_2 at 473 K. Still, pre-treatment by evacuation at 473 K was very slow, indicating that large quantities of water were again present. During the evacuation procedure, most water could be removed, but re-exposure to ambient air again led to significant amounts of adsorbed water, which became evident from a weight loss below 473 K of several per cent of the total mass, as determined from TGA. This is an indication that, despite modification, the bulk of most materials had remained hydrophilic. This also became clear from the three-phase contact angles with water: these were too small for formation of a stable water drop, and could therefore not be assessed reliably, even after modification. Possibly, the water droplet interacts with the underlying layers and not only with the top layer.

14

However, a hydrophobising effect of similar treatments has been observed from the ratio of permeabilities of (nonpolar) toluene and (polar) water, which increased slightly with the extent of modification from 0.6 for pure γ-Al_2O_3 to 1.1 for alumina modified by TCMS [11].

From the *C*-values of the BET fits, which are an indication of the strength of the adsorbate-adsorbent interaction, more information on the surface polarity was obtained. As the N_2 molecule interacts quite strongly with polar surface groups (e.g. OH-), high values indicate a hydrophilic surface. Clearly, CTMS/toluene and TCMS led to materials with the lowest *C*-values and thus have the most hydrophobic surfaces. Unmodified alumina also exhibits a rather low value, but this can be explained by the high pre-treatment temperature of 773 K, which also leads to a lower hydroxyl content and is therefore not directly comparable. Exposure to the water-containing liquids following the same procedures, but without silanes, gave *C*-values of around 180, showing a clear difference with most of the modified samples.

Adsorption isotherms of Ar did not reveal differences in *C*-values between the samples. The values were low in all cases (around 40), which could be anticipated, as Ar is a noble gas that is not involved in polar interactions. The adsorption / desorption isotherms of Ar further led to similar conclusions as for N_2 and did not provide additional structural information.

4. Conclusions

For γ-Al_2O_3 with a pore diameter of about 4 nm, we have shown that modification with especially chloromethylsilanes is very effective. The pore size and pore volume

15

remained largely preserved and modification was most homogeneous, as no steric hindrance of bulky groups occurred in the small mesopores. For CTMS, toluene as a solvent led to a much higher extent of modification than ethanol. Both CTMS and DCDMS were found to be suitable for homogeneous modification without extensive blockage of the pores. Application of TCMS led to polymerisation and thus to blockage of both micro- and mesopores. Inhomogeneous modification was also found for silanes with bulky alkyl groups, leading as well to loss of both microporosity and mesoporosity with respect to N_2 adsorption. Modification with these reagents occurred predominantly at the outside of the material. The distribution of the deposited silane on the material was found to be dependent on the homogeneity of the silane/solvent mixture. Factors that contributed to the homogeneity were temperature and whether or not water was added to the toluene solvent. Variation of the solvent and preparation procedures can be applied for further fine-tuning of the extent of modification. For high-temperature applications in membranes, post-modification of the external membrane surface with silanes with bulky organic groups after CTMS-modification of the membrane bulk can be envisaged to further increase permeance of nonpolar vs polar molecules.

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16

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17

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18

	Silane	Solvent	Temperature (K)	Time (h)
A1	$(CH_3)_3CSi(CH_3)_2Cl$	Toluene	298	24
A2	$(CH_3)_3CSi(CH_3)_2Cl$	Toluene + 5 wt% H_2O	323	12
A3	$(C_6H_5)_3SiCl$	Toluene	298	24
A4	$(C_6H_5)_3SiCl$	Toluene + 5 wt% H_2O	323	12
A5	$(CH_3)_3SiCl$	Toluene + 5 wt% H_2O	323	12
A6	$(CH_3)_3SiCl$	Ethanol + 5 wt% H_2O	298	12
A7	$(CH_3)_2SiCl_2$	Ethanol + 5 wt% H_2O	298	12
A8	$(CH_3)SiCl_3$	Toluene + 5 wt% H_2O	323	2.5

Table 1: Preparation procedures for modified γ-Al_2O_3 flakes.

19

Sample	Silane, conditions	$\Delta m/m_{end}$ (%)	v_p (cm^3/g)	$A(N_2)$ (m^2/g)	C	$A(CO_2)$ (m^2/g)	Mean d_p (nm)	d_p BJH (nm)
A	None	4	0.319	258	96	154	4.94	4.19
A1	(CH$_3$)$_3$CSi(CH$_3$)$_2$ Cl	27	0.141	216	157	121	2.62	3.6
A2	(CH$_3$)$_3$CSi(CH$_3$)$_2$ Cl	27	0.124	229	104	155	2.17	3.23
A3	(C$_6$H$_5$)$_3$ SiCl	26	0.047	70	-	150	2.67	-
A4	(C$_6$H$_5$)$_3$ SiCl	28	0.127	220	154	139	2.32	3.36
A5	(CH$_3$)$_3$ SiCl	28	0.230	276	79	131	3.33	4.07
A6	(CH$_3$)$_3$ SiCl, EtOH	7	0.297	249	181	154	4.66	4.00
A7	(CH$_3$)$_2$ SiCl$_2$, EtOH	9	0.289	268	150	142	4.33	3.99
A8	(CH$_3$) SiCl$_3$	12	0.224	216	89	-	4.16	3.81

Table 2: Analytical data (relative weight change above 473 K, pore volume at p/p_0= 0.95, N$_2$ surface area, C-value of the BET fit, CO$_2$ surface area, mean pore diameter and mean mesopore diameter from BJH fit) for γ-alumina materials (pure and modified with tert-butylchlorodimethylsilane, chlorotriphenylsilane and chloromethylsilanes). Liquid phase: toluene or EtOH (indicated).

Figure captions

Figure 1: N$_2$ physisorption isotherms for pure γ-alumina and materials modified with *tert*-butylchlorodimethylsilane and chlorotriphenylsilane (a) and with chloromethylsilanes (b). The dashed curves refer to samples A4 and A5.

Figure 2: Relation between mean pore diameter and extent of modification (corrected for the mass loss of A). The open and closed (except A3) symbols relate to the series addressed in the text.

Figure 3: Relation between pore volume and mean pore diameter (calculated from pore volume and surface area using eq. 6). For A3 no equilibrium was reached; this sample has a very low pore volume. The open and closed (except A3) symbols relate to the series addressed in the text. Linear relations are indicated by the trendlines.

Figure 4: SE Micrographs of (a) unmodified alumina A, and of modified aluminas (b) A6 and (c) A3. In the insets, parts of the micrographs have been enlarged twice.
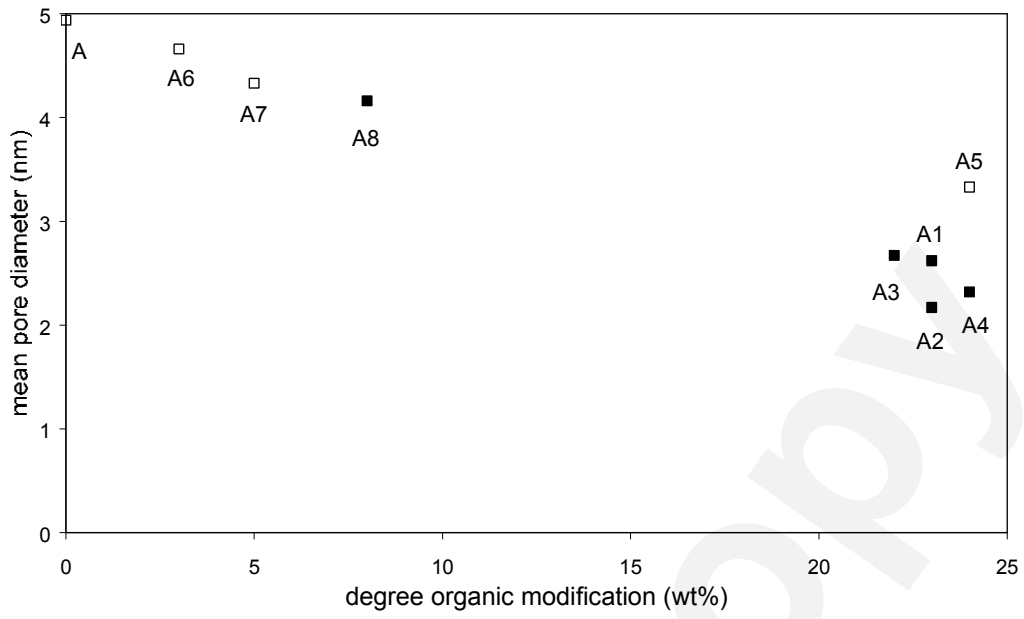
21

Figure 1a

Figure 1b

Figure 2

Figure 3

25

Figure 4a

Figure 4b

Figure 4c