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THERMOGRAVIMETRIC ANALYSIS OF γ-AMINOPROPYL-TRIMETHOXYSILANE ADSORBED ON SILICA SUPPORT

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Abstract

A comparative method based on thermogravimetry is applied in order to characterise chemically functionalised surfaces. The mass loss of silica modified with γ-aminopropyl-trimethoxysilane (γ-APS) adsorbed from a range of solvents is interpreted by considering the physically adsorbed water, the silanol groups and the organic solvent. DRIFT spectroscopy is used to analyse the binding structure and adsorption mechanism. The mass loss calculated from thermogravimetric analysis is found to be in agreement with the values obtained by classical elemental analysis. Thermogravimetric analysis is found to be a quick and reproducible method, which only requires a few milligram sample. The amount adsorbed seems to be primarily dependent on the solvation of the γ-aminopropyl-trimethoxysilane by the solvent. A good solvent prevents adsorption as shown when comparing the magnitude of the mass loss with the difference between the solubility parameters of the γ-APS and the solvents. Ethanol seems to influence the structure of the adsorbed γ-aminopropyl-trimethoxysilane film.

Keywords: adsorption, DRIFT spectroscopy, elemental analysis, γ-aminopropyl-trimethoxysilane, thermogravimetric analysis

Introduction

Oxide-immobilised organosilanes are of great importance. A common method to preconcentrate trace metals is to use chelating groups immobilised via silylation onto silica gel or particles used as supports. Such activated supports are used e.g. in phase-transfer catalysis, chemically modified electrodes, immobilised enzymes and metal ion chromatography, being only some of the applications appearing in the recent literature [1].

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The importance of aminoorganosilane modified silica is manifested in the vast array of literature published. Most papers [1–5] discuss the surface structure of the adsorbed aminoorganosilanes. Our interest is to analyse the adsorption quantitatively, i.e. to determine the amount adsorbed γ-aminopropyl-trimethoxysilane on silica.

There is a vast number of techniques available for the investigation of surface active molecules onto substrates. Most experimental methods have, however, an insufficient sensitivity to monitor the small amount adsorbate retained after washing the substrate with excess solvent. The most promising and straight forward techniques may be considered to be elemental analysis and thermogravimetric analysis.

The objective of this communication is to introduce thermogravimetry as a new quantitative analysis of organofunctionalised silicas with alkoxysilanes. It is a quick and reproducible method, which avoids the use of complex instrumentation and reagents. γ-aminopropyl-trimethoxysilane was adsorbed from different solvents in order to analyse the influence of the solvent in the adsorption process.

Experimental

Materials

The γ-aminopropyl-trimethoxysilane (γ-APS, A-1110, OSi specialities, now Witca) were used as supplied. Silica powder, (Grace Si S8MY) is reported to have A_{sp}=303 $m^2 g^{-1}$ and a particle diameter of 70 μm). Prior to use the silica was calcined at 420°C at ambient atmosphere for 20 h before use.

Diethyl ether, toluene and tetrahydrofuran (THF) (Lab Scan, AR) were dried by refluxing over sodium and benzophenon until the blue ketyl formed. Thereafter the solvents were distilled under nitrogen. Ethanol was dried in a 2 l flask containing 5 g of magnesium turnings, 0.5 g of iodine and 50 ml of ethanol. The mixture was warmed until a vigorous reaction occurred, then heating was continued for ~0.5 h. Up to 1 l of ethanol was added and the mixture refluxed for 1 h before distilling the ethanol off. The ethanol was stored on 3 Ĺ molecular sieves. Cyclohexane was dried over 3 Ĺ molecular sieves for at least 24 h before use.

Preparation of fully hydrolysed γ-APS

The γ-aminopropyl-trimethoxysilane was hydrolysed on a glass plate for five days.

Preparation of silica-immobilised silanes

Approximately 3.0 g of silica powder was dispersed in ca 19 g dry solvent with ca 1 g of γ-aminopropyl-trimethoxysilane. The reaction mixture was stirred frequently overnight at room temperature in order to ensure a full adsorption to the surface (rapid) as well as an absorption onto the porous interior (slow) of the particles [5]. Thereafter the particles were filtered and washed exhaustively with solvent. The product was dried for 5 h in vacuum at 50°C.

Characterisation

DRIFT spectroscopy measurements

Samples for diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy were made by mixing approximately 15% w/w sample with dry KBr in a Wig-L-Bug capsule for 2 min without the metal ball. The KBr mixed sample was filled in the DRIFT sample cup by gentle tapping.

A Perkin Elmer Spectrum 1000 equipped with an MCT detector was used for the DRIFT measurements. The spectral resolution was 4 cm^{-1}, and 100 scans were accumulated for each spectrum.

Elemental analysis

A Perkin Elmer CHNS/O Serie II 2400 was used for elemental analysis (EA). The sample is heated to 975°C and the gases are analysed at a somewhat lower temperature. The relative percentage of C and N was measured and reported.

Thermogravimetric measurements

A Netzsch Thermo Microbalance TG 209 is used for thermogravimetric (TG) measurements. The sample was first pre-treated at 70°C for 1 h to remove physisorbed water. After this the temperature was raised with 5°C per min to 900°C, where the sample is kept for 30 min. Nitrogen at a flow of 15 ml min^{-1} is used as purge gas. The sample mass is typically between 3.0 and 4.3 mg.

Results and discussion

Infrared spectroscopy: DRIFT-measurements

Before the spectroscopic analysis the modified substrate has to be cured or dried. The curing or drying may cause desorption of water and/or condensation of the adsorbed molecules, thus changing the structure of the modified surface. As a consequence, no data on the adsorption mechanism in the loading step can be obtained. It is important to be aware of the distinction between the loading and curing step. Waddel *et al.* [1] have shown that oven curing increase the stability of the product. They showed that a curing time of 3 h at 80°C is expected to be sufficient to transform all hydrogen bonds between γ-APS and silica to covalent bonds, thus providing a more accurate analysis of the amount adsorbed. Adsorption isotherms show that the amount used to treat silanes correspond to a multilayer siloxane film on the silica surface [6a, 7].

The bands at 3371 and 3301 cm^{-1} in Fig. 1 are the asymmetric and symmetric stretching of the NH_2 group of adsorbed γ-APS, respectively. The corresponding values for fully hydrolysed γ-APS are 3352 respectively 3272 cm^{-1}. Hydrogen bonding shifts these stretching vibration bands below 3370 and 3310 cm^{-1}, respectively [6b]. This indicates the formation of a polymerised aminopropylsiloxane for fully hydrolysed γ-APS. For adsorbed γ-APS there is some polymerisation and interaction be-

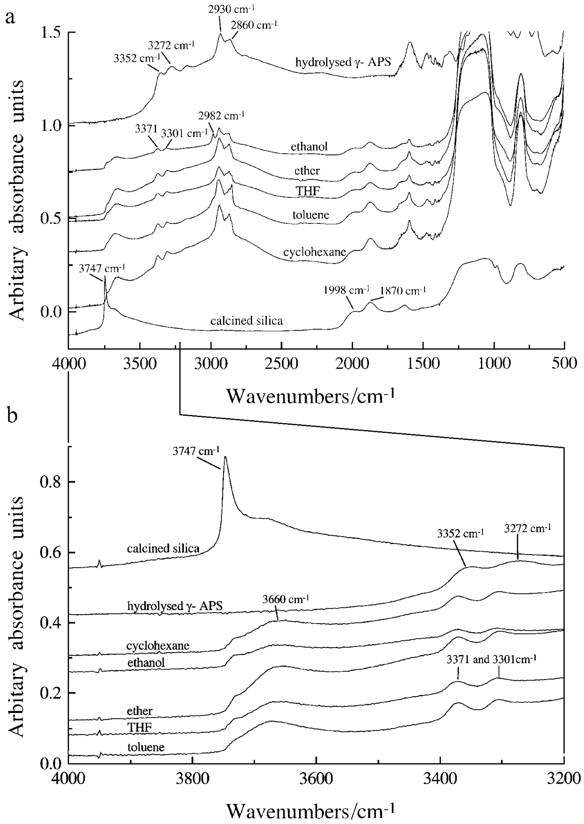

Fig. 1 A normal and expanded DRIFT spectrum of calcined silica, fully hydrolysed γ-APS, and γ-APS adsorbed onto silica from cyclohexane, ethanol, ether, tetrahydrofurane and toluene

tween Si–OH groups of silica and NH_2 through hydrogen bonding. It is also claimed that surface water promotes amine–surface interactions and orients the amino moieties towards the surface [6b].

Zero or blank samples, i.e. only solvent and silica, show no difference in the DRIFT spectra compared to the spectra of pure calcined silica. Therefore we conclude that no toluene, cyclohexane, nor ether is adsorbed. For THF, we can detect a peak at 1719 cm^{-1} in the blank sample. As γ-APS is adsorbed, this peak disappears. Therefore we conclude that no THF is adsorbed. The peak at 2982 cm^{-1} in Fig. 1 is assigned the OCH_2CH_3 group, and indicates that ethanol is adsorbed on to the silica surface. For ethanol, this peak is clearly visible both for the blank test and after γ-APS is adsorbed.

For a successful quantitative analysis with DRIFT there has to be a linear relationship between the relative reflectance function and the concentration of the sample. Furthermore, the peak area should be dependent on the particle shape, size and packing density [8]. The sample has to be homogeneous after dispersing with KBr and the sample height has to be uniform in the DRIFT accessory. In order to meet these requirements the sample preparation was repeated for at least five times and indeed reproducible alkane/ silica ratios were obtained, as shown in Table 1.

Table 1 The accuracy of the results obtained with DRIFT spectroscopy

Solvent	A_{alkane}/A_{Si}	St.dev.	Normalised (A_{alkane}/A_{Si})
cyclohexane	2.09	0.082	1.03
diethyl ether	2.22	0.058	1.10
ethanol	1.70	0.073	0.84
toluene	2.02	0.048	1.00
tetrahydrofurane	2.18	0.072	1.08

Murthy *et al.* [8] used the Kubelka-Munk function to relate reflectance response to the sample concentration. Smyrl *et al.* [9] on the other hand, claim that the Kubelka-Munk function suppresses weak peaks in favour of the more intense peaks and introduced an own function. We found that neither the Kubelka-Munk algorithm nor the function introduced by Smyrl *et al.* was suitable for us. Porro and Pattacini [10] have obtained quantitative results with DRIFT of silane treated clays without using the Kubelka-Munk correction. The key to their success was to use samples with low concentration and consequently low absorbance.

Investigations of the effect of silica particle size on the DRIFT spectrum indicate that the intensity of the Si–O–Si combination band at 1870 cm^{-1} was the least affected by particle size [7]. Hence, it was chosen as the reference band. We found that the unconverted absorbance for the sum of the peak areas at 2935 and 2872 cm^{-1} was the most suitable for alkane quantification. These bands are assigned as the symmetric and the asymmetric stretching vibrations respectively of the CH_2 groups in the propyl chain [5].

Elemental analysis

In elemental analysis (EA) the sample is combusted and the burn-off products analysed. The relative percentages of C and N are reported. From the percentage, the amount of silane per gram of modified silica may be derived directly. To calculate the silane loading per gram of pure silica, the molar mass of the deposited molecule is needed. γ-APS may be deposited in four configurations. The trimethoxysilane group can be adsorbed either in mono-, bi-, or tridentate form to the silica surface or the amine group may bound to the surface. Each configuration has unequivocally defined molar masses. Waddel *et al.* [1] suggested a bonding model where $-CH_2CH_2CH_2NH_2$ sticks up from the silica surface. Cestari and Airoldi [11] also claim that aminopropyl is released during heating. They concluded that the molar C/N ratio is 4.3 for ethanol and varies between 3.5–4.0 for the other solvents.

From the models suggested it may be assumed that 8H and 3C atoms per N-atom (i.e. an aminopropyl group) is desorbed upon heating. The amount of γ-APS adsorbed can thus be estimated using Eq. (1a):

$$\text{wt\% } (\gamma\text{-APS})=[C/N\cdot M_W(C)+M_W(N)+8\cdot M_W(H)\cdot \text{ wt\%}(N)/14 \qquad (1a)$$

$$\text{wt\% } (\gamma\text{-APS})=[3\cdot M_W(-(CH_2)_3NH_2)+(C/N\text{-}3)\cdot M_W(-(OCH_3))]^{*}\text{wt\%}(N)/14 \qquad (1b)$$

The results are collected in Table 2.

Table 2 Wt% γ-APS adsorbed onto silica calculated according to Eqs (1a and b)

Solvent	C/N ratio	wt% N	γ-APS/wt% (1a)	γ-APS/wt% (1b)
cyclohexane	3.47	1.45	6.6	7.5
diethyl ether	3.50	1.43	6.5	7.5
ethanol	4.27	1.03	5.4	7.2
toluene	3.72	1.29	6.1	7.4
tetrahydrofurane	4.01	1.25	6.3	8.0

However, since the C/N-ratio exceeds the number (3) expected for a propyl group, the excess mass thermally desorbed must contain contributions from unhydrolysed methoxy groups. We have, indeed, been able to identify a small amount of such groups in seemingly fully hydrolysed γ-APS solutions using ^{1}H-NMR (PMR). The amount silane adsorbed may thus be corrected to account for both the aminopropyl group ($M_W \approx 58$ g mol^{-1}) and the methoxy group ($M_W \approx 31$ g mol^{-1}) as done in Eq. (1b). The results are reproduced in Table 2.

Thermogravimetric analyses

A temperature programme where the sample was first pre-treated at 70°C for 1 h to remove physisorbed water was used in the experiments. After this the temperature was raised with 5°C per min to 900°C, where the sample is kept for 30 min. The mass loss is calculated between the isothermal segments at 70 and 900°C. Calcined silica is used as reference, and the mass loss between 420 and 900°C is subtracted from the obtained result. The mass losses observed are presented in Fig. 2. The repeatability of the TG measurements was very good, two measurements differ at the most by 5%.

The heat treatment will sucessively remove the solvent, the isolated OH groups and the hydrogen bonded OH from the silica [12]. At 900°C no mass loss is observed. Therefore we conclude that all organic substance is desorbed, which also agrees with our DRIFT measurements, illustrated in Fig. 3.

A summary of the thermal analysis results is given in Table 3. It is obvious that a reasonably good correlation is found with the DRIFT and the elemental analysis results. In order to rationalise the results the amount γ-APS adsorbed was compared

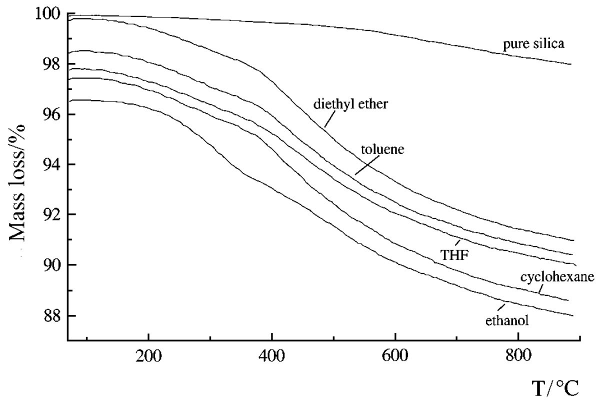

Fig. 2 Mass loss as a function of temperature for pure silica and silica with γ-APS adsorbed from different solvents

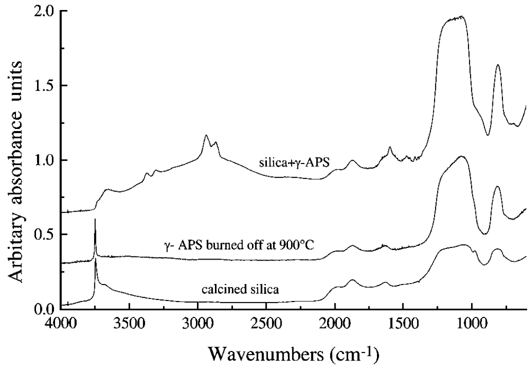

Fig. 3 DRIFT spectra of γ-APS adsorbed onto silica and thermally desorbed up to 900°C

with the solubility parameter of the solvents (Table 3). It has recently been shown [13] that a poor adsorption of silane is related to a small difference between the solubility parameter of the silane and the solvent, respectively. The reason is that if the silane is the effectively solvated by the solvent there is no driving force for adsorption. The absolute value of the difference in solubility parameters are closely related to the enthalpic or the activity factor contribution to the regular solution Gibbs free energy [14]. For the solvents investigated the solubility parameter grows in the following sequence; diethyl ether ($15.1\cdot10^{-3}\sqrt{\mathrm{J}}\ \mathrm{m}^{-3}$), cyclohexane ($16.8\cdot10^{-3}\sqrt{\mathrm{J}}\ \mathrm{m}^{-3}$), toluene ($18.2\cdot10^{-3}\sqrt{\mathrm{J}}\ \mathrm{m}^{-3}$), tetrahydrofurane ($18.6\cdot10^{-3}\sqrt{\mathrm{J}}\ \mathrm{m}^{-3}$), and ethanol ($26.0\cdot10^{-3}\sqrt{\mathrm{J}}\ \mathrm{m}^{-3}$). A calculation of the solubility parameter of γ-APS may be done by summing up the contributions of the groups [15]. The value found was $17.83\cdot10^{-3}\sqrt{\mathrm{J}}\ \mathrm{m}^{-3}$ which falls between cyclohexane and tetrahydrofurane. In Table 3 the mass γ-APS adsorbed is arranged in order of the magnitude of the difference in solibility parameter between the γ-APS and the solvent. The relative mass adsorbed is normalised by dividing each value with the mass adsorbed from toluene.

Table 3 Wt% adsorbed γ-APS on silica measured with different methods related to the difference between the solubility of the γ-APS and the solvents

Solvent	TG	Normalised TG	Normalised EA (Table 2)	Normalised DRIFT (Table 1)	$\Delta\delta$ $(\mathrm{J\ m^{-3}})^{1/2}\cdot 10^{-3}$
toluene	5.8	1.00	1.00/1.00	1.00	–0.37
tetrahydrofurane	5.9	1.02	1.03/1.08	1.08	–0.77
cyclohexane	6.1	1.05	1.08/1.01	1.03	1.03
diethyl ether	6.6	1.14	1.07/1.01	1.10	2.73
ethanol	5.9	1.02	0.88/0.97	0.84	8.17

The results seems to be quite reasonable, since it is well known that toluene and tetrahydrofurane are particularly good solvents for silanes. The cyclohexane is, in the light of these results, still acceptable ($\Delta|\delta|<2\ (\mathrm{J\ m^{-3}})^{1/2}\cdot 10^{-3}$), while the solvation diminishes from diethyl ether to ethanol.

Although the overall trend is clear there are some accidental discrepancies found depending on the method used. The best correlation with the solubility parameter is obtained for thermogravimetry. DRIFT and elemental analysis (Eq. (1a)) agree closely showing only one discrepancy which may be due to the different experimental conditions. The elemental analysis corrected for the methoxy group adsorption (Eq. (1b)) was less successful in reproducing the general trend.

The special feature of the ethanol system is particularly apparent and requires further analysis. Since the termogravimetry gave the most straightforward result the mass loss was derived with respect to the temperature and plotted with the pure calcined silica and toluene system as a reference *vs*. the heating temperature.

The desorption of water occurs at 230–300°C and the desorption of γ-APS reaches a maximum at ca. 430°C. As shown in Fig. 4 very small differences were found between the toluene and the other solvent systems. However, since cyclohexane is a less good solvent than toluene the amount of γ-APS desorbed at 400–450°C increases. The opposite is true for tetrahydrofurane, where the mass loss is smaller than for the toluene system. For the diethyl ether system a considerable broadening of the thermal peak is observed indicating a range of binding states, which may explain the enhanced adsorption. Finally, for ethanol the main peak has shifted to around 300°C. Most probably a considerable amount of ethanol coadsorbs to the silica particles displacing a part of the γ-APS from the surface. This was also apparent from the DRIFT spectra (Fig. 1). Consequently the mass of γ-APS desorbed diminishes (Table 3). However, since ethanol adsorbed on the pure silica particles is completely desorbed during the drying (50°C, 5 h, vac.) and the preheating (70°C, 1 h) stages either the ethanol is intercalated in the silane network or then the silane film structure is strongly modified by the ethanol. A rearrangement of the silane network by methanol was observed in a previous investigation [13]. Since the solubility parameter is enhanced the more condenced the silane is, ethanol and methanol become superior solvents for the polymerised species. Consequently, not only the absolute value of the difference between the solubility parameters, but also the sign is important.

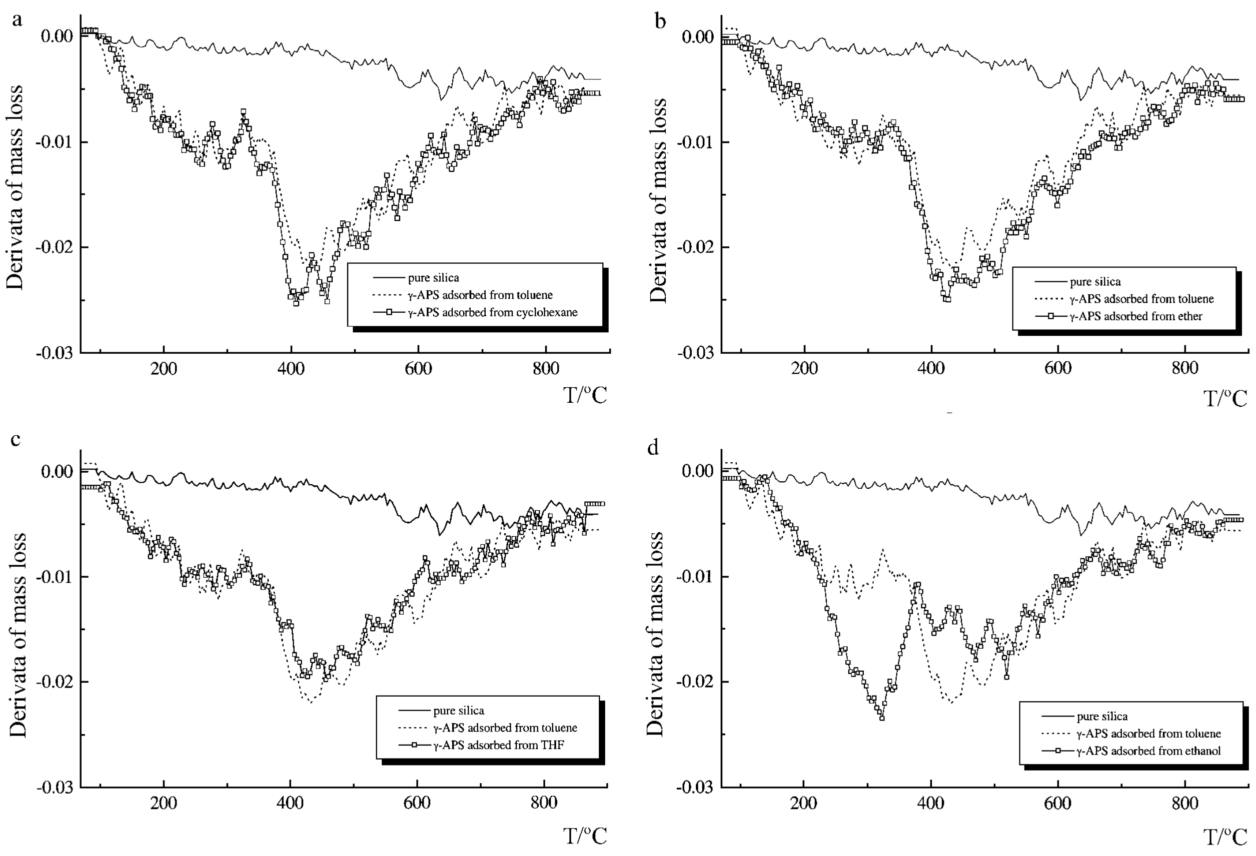

Fig. 4 The derivative of the mass loss of γ-APS adsorbed from the different solvents with respect to the temperature plotted as a function of the desorption temperature. The desorption of the solvents from pure silica and the γ-APS adsorbed from toluene are given as references

Conclusions

There is a rather good agreement between the results obtained with thermogravimetry, elemental analysis and DRIFT spectroscopy, despite the widely varying methods of analysis.

The adsorption seems to be primarily dependent on the solvation of the γ-APS by the solvent. The absolute difference between the solubility parameter of the silane and the solvent may thus be used to predict relative solubilities and/or probability for adsorption.

Thermogravimetric analysis was particularly useful when distinguishing the different adsorption mechanisms. The mass loss indicates a competitive adsorption of ethanol or a rearrangement of the γ-APS network as also shown in the DRIFT spectrum.

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