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An FT–IR Study of the Chlorination of γ-Alumina Surfaces

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Abstract

Surface chlorination of two aluminas (Degussa and Condea; $S_{BET} = 100\ m^2\ g^{-1}$) has been realized either by reaction of $CHCl_3$ on an alumina pellet inside the IR cell or by flowing $HCl_{(g)}$ on alumina powder for one hour outside the IR cell. The FT–IR analysis of the chlorinated samples showed that the bands assigned to OH groups, specially in the range of higher wavenumbers (3800–3700 cm^{-1}), are sensitive to the presence of chlorine on the surface taking the place of the more basic surface OH groups by substitution reaction. The nature of the additive products influenced the bands in the 1600–1200 cm^{-1} region. The evolution of surfaces rehydratation showed that the chlorinated aluminas are more stable than the raw ones with respect to the presence of H_2O on the surface. The hydrolysis modified the surfaces of both raw Al_2O_3, whereas the surfaces of the chlorinated aluminas were restored after thermal treatment at 870K. © 1998 Published by Elsevier Science Limited.

Résumé

La chloration de surface de deux alumines (Degussa et Condea) de surface spécifique de 100 $m^2\ g^{-1}$ a été réalisée soit par réaction de $CHCl_3$ avec la surface à l'intérieur de la cellule infrarouge soit par passage de $HCl_{(g)}$ sur la poudre d'alumine durant une heure à l'extérieur de celle-ci. L'étude infrarouge des surfaces chlorées montre la présence de réactions de substitution entre les groupes OH de la surface et le chlore des deux agents chlorants. Ce sont les groupes OH les plus basiques qui réagissent. La nature des additifs modifie aussi le spectre dans la région 1600–1200 cm^{-1}. Une réhydratation a révélé que les alumines ainsi chlorées sont plus stables que celles non traitées en ce qui concerne l'action de la molécule H_2O sur la surface. En effet l'hydrolyse affecte la surface des deux alumines brutes, alors que celle des alumines chlorées est restaurée après chauffage à 870K.

Introduction

Alumina finds application as an adsorbant and as a catalyst or catalyst support in a wide variety of processes in chemical industries.[1–3] But it is well known that the physicochemical and catalytic properties can be modified by the presence, in the surface layer, of variable amount of ions—impurities or addition. So, the surface fluorination[4–7] as well as the surface chlorination[8–11] change the acid-basic properties of transition aluminas, in so far as the acid strength increase, thus leading to a higher reactivity and selectivity of the sample. These surface impurities could also be useful to promote sintering processes which start from surface reactions.

In the present work, we have chosen two aluminas prepared from different synthesis and consequently having different impurities or additions. These samples were subject to a chlorination. Our aim was to perform an infrared study of both aluminas, treated or not, in order to analyze and compare the effect of the surface treatment of these compounds in relation with their surface structure and properties.

Experimental

Two commercial aluminas with relatively high surface areas (100 $m^2\ g^{-1}$) were used: (i) Degussa, C–Al_2O_3, synthesized by flame hydrolysis of $AlCl_3$, almost free from metal ion impurities, but containing some amounts of chlorine (less than 0·5% W/W); (ii) Condea obtained by thermal dehydration of boehmite, free from chlorine but containing

10ppm of Na^+ ions. X-ray diffraction indicated that both structures were in the γ phase.

All infrared experiments were carried out using a stainless steel grid (Ø = 2 cm) on which the compound was lightly pressed into the form of self-supporting disc. These pellets were mounted in a standard infrared cell (Fig. 1) connected to a vacuum line allowing in situ experiments. The grid allowed a good heating conduction; the temperature calibration of the pellet was checked, using an infrared camera, from the emittance of a grid supported blackened ceramic. Activation consisted in heating up under dynamical vacuum at about 10^{-5} hPa and then in cooling down to room temperature. This first operation aim was to expel the physisorbed water from the surface.

Chlorination with HCl was performed at room temperature with dry gas produced from the reaction between H_2SO_4 and NaCl. The powder was put back into the air before being introduced in the infrared cell and was activated under dynamical vacuum.

Chlorination of the activated aluminas with $CHCl_3$ was carried out *in situ* at room temperature, according to previous works.[11] After activation at 870 K under dynamical vacuum, the raw material was exposed to gaseous chloroform (P No. 15 hPa) for 12h at 300K; then, the gas was evacuated in order to remove the excess of unreacted reactant, as well as the surface reaction products.

In situ experiments were performed under dynamical vacuum (10^{-5} hPa), at various temperatures (between 300 and 870 K). All the absorption spectra were recorded after returning at room temperature using a FT–IR spectrometer (Nicolet 5DX) with a 4 cm^{-1} resolution after 200 scans over the 4000–400 cm^{-1} range.

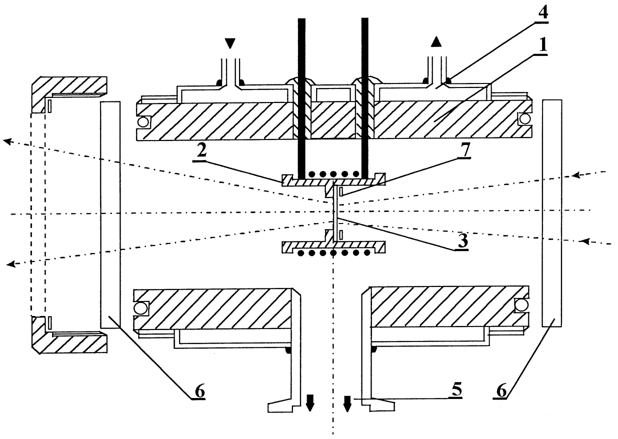


Fig. 1. Schematic cross section of the infrared cell for high temperature (up to 870K) activation and reaction under vacuum or controlled atmosphere. (1) Stainless steel cell body, (2) internal furnace with heating element thermocoax ®, (3) convergence of the infrared beam on the sample through KBr windows (6), (4) external water cooling, (5) vacuum line (10^{-6} hPa) or gas inlet, (7) sample holder.

The adsorbate D_2 (Alphagaz 99·99%) was used without further purification. D_2 was introduced in the cell under 100 hPa at 870 K. This high temperature allowed to observe easily the kinetic of the surface H–D exchange. After 1 h, D_2 was evacuated and the temperature returned back to 300 K.

Results and Discussion

When the activation was performed at 870 K, the spectrum of the Degussa Al_2O_3 pellet showed a broad band including two individual peaks at 3787 and 3778 cm^{-1}, and a component at 3722 cm^{-1} followed by a very strong absorption located at 3675 cm^{-1} with a shoulder at 3596 cm^{-1} (Fig. 2). According to our previous work,[12,13] bands at 3787 and 3778 cm^{-1} were assigned to terminal OHs over one tetrahedrally coordinated Al ion, either in a non vacant environment or near a cation vacancy, respectively; the band at 3722 cm^{-1} was assigned to a terminal OH over an octahedrally coordinated Al ion, while the bands at 3675 and 3596 cm^{-1} were assigned to bridging and triply bridging OHs, respectively. These assignments have been confirmed by further studies on different spinel-type and corundum-type metal oxide powders.[14]

Besides, when D_2 gas was introduced into the cell, only the OH groups located on the surface were quickly exchanged into OD groups in the ratio ν_{OH}/ν_{OD} (No. 1356) according to harmonic oscillator approximation. The deuteriation confirmed the assignment of these bands to different types of OH groups on the surface and none of them were in the bulk.

Similar bands of OH vibrators were also observed after activation at 870 K on Al_2O_3 Condea surface (Fig. 3). The maxima and their assignments are reported in Table 1.

The main difference between the two aluminas was the presence of two monocoordinated OHs bonded to Al_{IV} for the Degussa Al_2O_3, while only one type was observed on Condea Al_2O_3 surface.

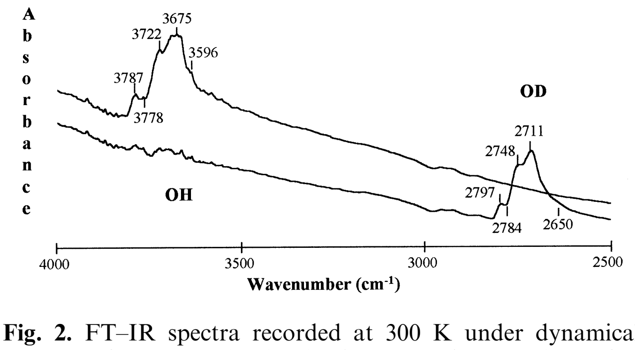


Fig. 2. FT–IR spectra recorded at 300 K under dynamical vacuum of Degussa alumina in the OH and OD regions after activation at 870 K.

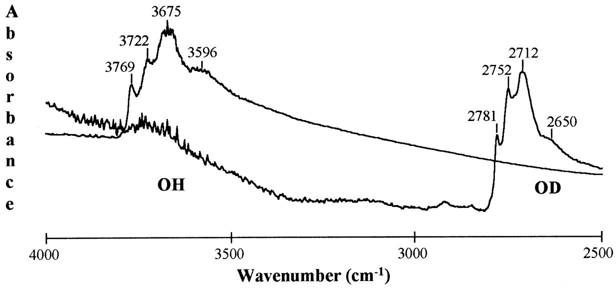


Fig. 3. FT–IR spectra recorded at 300 K under dynamical vacuum of Condea alumina in the OH and OD regions after activation at 870 K.

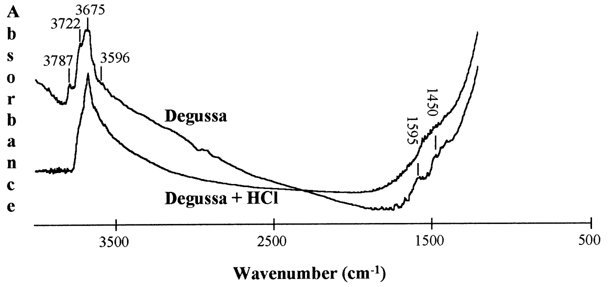


Fig. 4. FT–IR spectra recorded at 300 Kunder dynamical vacuum of raw and treated by HCl Degussa alumina after activation at 870 K.

After treatment with HCl the spectrum of Degussa alumina (Fig. 4) showed the disappearance of the IR absorption bands of the free OH groups around 3790 cm^{-1} (Al$_{\mathrm{IV}}$), originally present on this alumina sample, and the decrease of the intensity and of the width (calculated by deconvolution) of the band near 3720 cm^{-1} (Al$_{\mathrm{VI}}$). Other absorption bands measured in the 1600 and 1400 cm^{-1} region, which could be assigned to carboxylate species (Fig. 4), also disappeared after HCl treatment.

The treatment of the same Degussa alumina sample with $CHCl_3$ (Fig. 5) also reduced the intensity of both OH bands due to monocoordinated OH groups, and induced a very strong absorption centred at 3487 cm^{-1}, which could be assigned to perturbed OHs of water. By evacuation and heating at 470 K the band at 3487 cm^{-1} decreased, with the appearance of bands due to free OH groups at 3729 and 3675 cm^{-1}. Moreover three other bands were observed at 1594, 1455 and 1392 cm^{-1} in a region typical for carboxylate species. A ν_{CH} band at 2973 cm^{-1} persisted under these conditions, proving that $CHCl_3$ was not completely desorbed while the shoulder at 2920 cm^{-1}, associated with bands at 1593 and 1392 cm^{-1}, suggested that formates existed on the surface.

After thermal treatment at higher temperature up to 870 K, the ν_{CH} bands disappeared and bands due to free OH vibrators were again observed. The maximum (3675 cm^{-1}) was associated with bridging OH groups. The band assigned to terminal OHs linked to Al$_{\mathrm{IV}}$ at 3787 cm^{-1} was absent, while a new shoulder in the 3675 cm^{-1} band was detected at 3697 cm^{-1} which could be assigned to new bridging OH groups.

The three bands assigned to carboxylate species between 1570–1400 cm^{-1} were reduced into two at 870 K with a slight shift which would mean that an evolution of the coordinence state of formate surface occurred during heating over 470 K.

Chlorination of the Condea alumina gave similar results (Figs 6 and 7), i.e.:

- disappearance of the band at the highest wavenumbers (OH monocoordinated to tetrahedral Al^{3+});
- large decrease of the intensity in the region of the OH monocoordinated to Al$_{\mathrm{VI}}$ near 3720 cm^{-1}.

According to Baumgarten[15] the reactivity of alumina surfaces towards HX molecules (F, Cl, Br, I) highly suggested that the substitution of surface OH groups by halogenide ions should be easier for the most basic OH groups. Our experimental

Table 1. Experimental frequencies (cm^{-1}) of ν_{OH} and ν_{OD} bands in Al_2O_3 Degussa and Condea and their assignments (the splitting of the linear A$_{\mathrm{IV}}$ is due to cation vacancies in the neighboring of some sites)

Degussa		*Condea*		*Co-ordination*
ν_{OH}(cm^{-1})	ν_{OD}(cm^{-1})	ν_{OH}(cm^{-1})	ν_{OD}(cm^{-1})	
3787	2797	—	—	Linear Al $_{\mathrm{IV}}$
3778	2784	3769	2781	Linear Al$_{\mathrm{IV}}$
3722	2748	3722	2752	Linear Al$_{\mathrm{VI}}$
3675	2711	3675	2712	Bridging
3596	2650	3596	2650	Triply-bridging

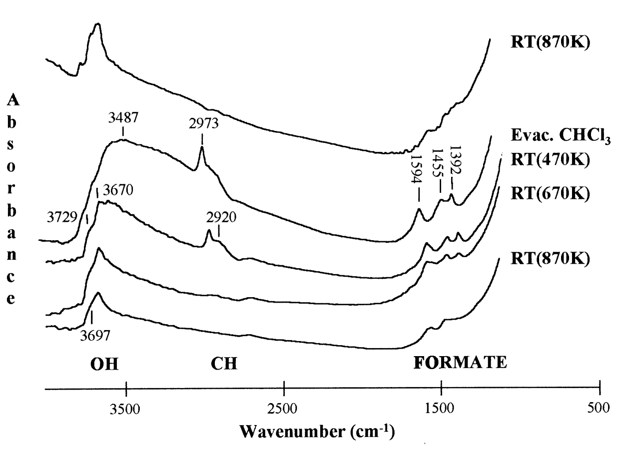


Fig. 5. FT–IR spectra recorded at 300 K under dynamical vacuum of raw and treated by $CHCl_3$ Degussa alumina after evacuation of $CHCl_3$, 470, 670 and 870 K.

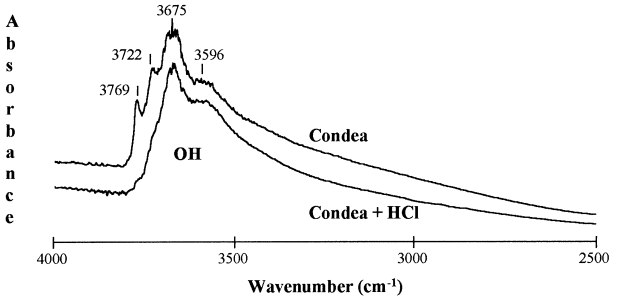
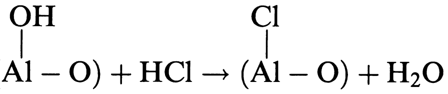


Fig. 6. FT–IR spectra recorded at 300 K under dynamical vacuum of raw and treated by HCl Condea alumina after activation at 870 K.

results showed that the OH groups monocoordinated to Al_{IV}, which should be the most basic according to Morterra's study,[16] were very active with respect to chlorination, as also observed by Lavalley.[17] Their disappearance after treatment with HCl indicated that a substitution reaction took place in agreement with the mechanism proposed by Kytökivi:[18]



$$\overset{OH}{(Al - O)} + HCl \rightarrow \overset{Cl}{(Al - O)} + H_2O$$

The broad absorption band observed at 3500 cm^{-1} after reaction of HCl, eliminated by activation under vacuum, was due to water formation which agreed with this mechanism.

The mechanism of chlorination by $CHCl_3$ was more complex, but, according to our experimental results, it should involve only the most basic monocoordinated OHs. Formates chemisorbed on the surface were formed still persisting at the highest temperature of activation (870 K).

The fact that in both aluminas chlorination affected the higher frequency OH region could be considered as a confirmation of the assignment of both bands measured in this region for the Degussa alumina (Fig. 2) to terminal OHs over tetrahedrally coordinated Al ions, as proposed by Busca *et al.*[12,13] rather than on Al ions of different coordination (Al_{VI} and Al_{IV}) as proposed by Knözinger and Ratnasamy.[19]

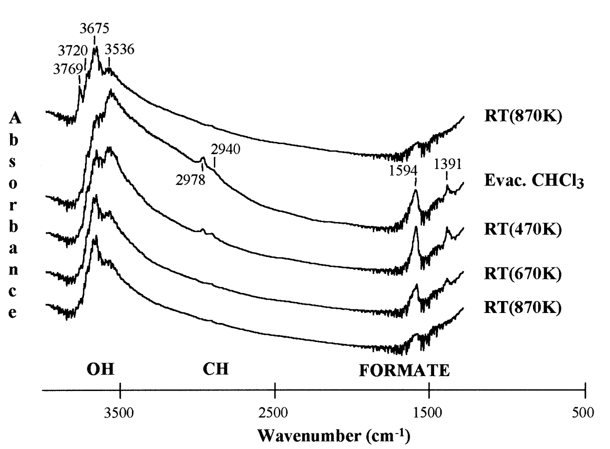
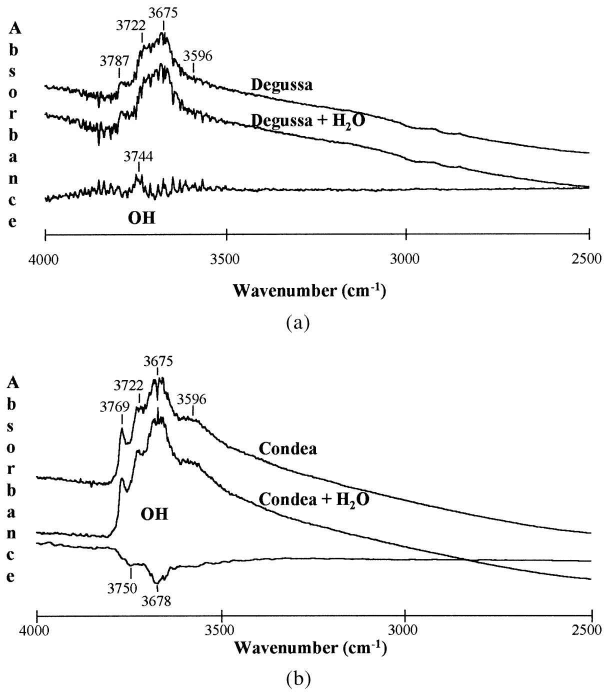


Fig. 7. FT–IR spectra recorded at 300 K under dynamical vacuum of raw and treated by $CHCl_3$ Condea alumina after evacuation of $CHCl_3$, 470, 670 and 870 K.

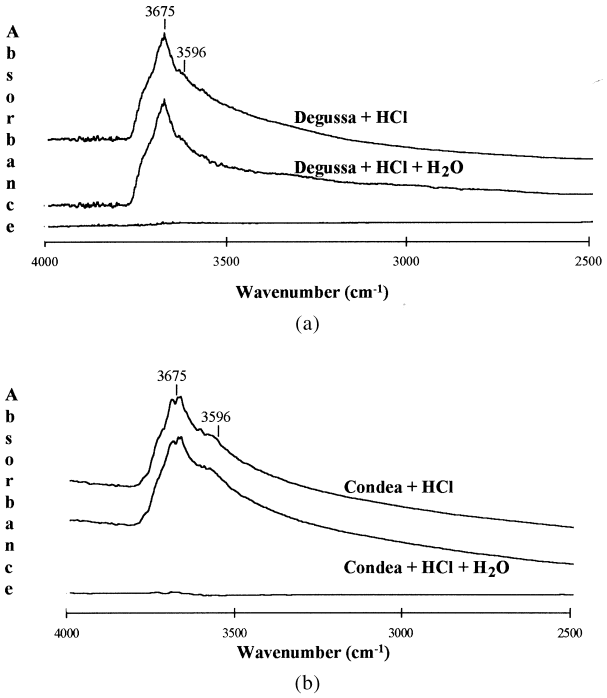
Kytökivi[18] has also shown by quantum chemical calculations that chlorinated surfaces of alumina were more stable than hydroxylated surfaces and water did not hydrolyse the Al–Cl bonds formed. This was confirmed by hydrolysis experiences (Figs 8 and 9) on our aluminas. Whereas the hydrolysis, at ambient temperature, modified the surface of both raw Al_2O_3 (Fig. 8(a) and (b)), the surfaces of the chlorinated aluminas were restored after the thermal treatment (Fig. 9(a) and (b)). By this way, we could observe that surfaces of raw aluminas were not modified in the same way by hydrolysis: a new band at 3744 cm^{-1} was observed for the Degussa alumina which had to be assigned to OH groups not exposed on the surface as they were not sensitive to the deuteriation. As for the Condea alumina, which was more acidic because of the more intense tricoordinated OH band, we observed some negative OH bands on the difference spectra of Fig. 8(b), probably due to modifications of the intensity of the OH bands affecting the intensity difference.



(a)

(b)

Fig. 8. (a) FT–IR spectra in the OH region recorded at 300 K under dynamical vacuum of raw Degussa alumina after heating at 870 K: before and after treated by H_2O vapor and the difference spectrum. (b) FT–IR spectra in the OH region recorded at 300 K under dynamical vacuum of raw Condea alumina after heating at 870 K: before and after treated by H_2O vapor and the difference spectrum.



(a)

(b)

Fig. 9. (a) FT–IR spectra in the OH region recorded at 300 K under dynamical vacuum of treated by HCl Degussa alumina after heating at 870 K: before and after treated by H_2O vapor and the difference spectrum. (b) FT–IR spectra in the OH region recorded at 300 K under dynamical vacuum of treated by HCl Degussa alumina after heating at 870 K: before and after treated by H_2O vapor and the difference spectrum.

Conclusion

The alumina surfaces can be chlorinated by reaction with HCl or $CHCl_3$. This chlorination occurs on monocoordinated OH groups linked to tetrahedral or octahedral aluminium atoms. The Condea surface is poorly reactive whereas the Degussa one is more reactive. The stability of the chlorinated surfaces has been confirmed by hydrolysis experiments.

Acknowledgements

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