Journal of the European Ceramic Society **18** (1998) 1753–1757

PII: S0955-2219(98)00113-7
0955-2219/98/$—see front matter

FT-IR Study of CH_3OH Adsorption on Chlorinated γ-Aluminas

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(Received 24 December 1997; accepted 9 April 1998)

Abstract

In a previous paper, the surfaces of as-received or Cl-treated aluminas were studied. In this work, the action of CH_3OH molecules on pure or Cl- treated alumina was analyzed using FT-IR spectrometry. The methoxylation of all surfaces was observed through the presence of OCH_3 linked to Al_{VI} or Al_{IV}. Above 470 K, the methoxy group tended to disappear and a new species, formate, was found. The positions of $\nu(CH_3)$ frequencies depended on the production process of alumina powders as well as on their treatment. The modification of the evolution into formate at the different surfaces was discussed. © *1998 Elsevier Science Limited. All rights reserved*

Résumé

Dans un premier article, nous avons étudié les surfaces de deux alumines, différemment traitées par le chlore et non traitées. Dans cette partie, nous analysons par spectrométrie infrarouge (FT-IR) l'action du méthanol sur ces mêmes alumines. La méthoxylation de toutes ces surfaces intervient par fixation du groupement OCH_3 sur les sites Al_{VI} or Al_{IV}. Ces groupes méthoxy tendent à disparaître alors qu'il se forme une nouvelle espèce: des formates. Les fréquences $\nu(CH_3)$ dépendent à la fois du procédé d'obtention de l'alumine et de son traitement ultérieur. Nous discutons la formation des formates sur ces différentes surfaces.

1 Introduction

The understanding of the interaction of alcohols with oxide surfaces is relevant with respect to heterogeneously catalysed reactions such as dehydrogenation or dehydratation.[1–5] Many works on the alcohols adsorption on different oxides have been carried out[6–10] but no investigation on the adsorption behaviour of alcohols on chlorinated alumina has been reported in the literature.

In a previous study,[11] the chloride ions were introduced on two different aluminas so as to show the modification of the surfaces through the analysis of OH vibrational groups. In the present work, we studied the adsorption of methanol vapor at room temperature on samples of either raw or chlorinated aluminas, using FT-IR spectroscopy, in order to identify the effect of chlorination on chemisorbed methanol and on its evolution on the surface.

2 Experimental

Two commercial alumina powders with relatively high surface areas ($100\,m^2\,g^{-1}$) were used : (i) Degussa C, synthesized by flame hydrolysis of $AlCl_3$, almost free from metal ion impurities, but containing substantial amounts of chloride (0·5% W/W); (ii) Condea, obtained by thermal dehydration of boehmite, free from chloride but containing Na^+ (10 ppm) and Ca^{2+} (8 ppm) cations. These materials when studied 'as manufactured' without surface treatment are refereed as 'raw'.

Chlorination was carried out either *ex situ*, by action of HCl gas on Al_2O_3 powder during 1 h—the newly formed powder was then introduced into the cell and activated up to 870 K in vacuum—or *in situ* by reaction of $CHCl_3$ gas at room temperature on the activated sample.

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Samples were lightly pressed so as to obtain a self-supporting disc on a stainless steel grid ($\phi = 2$ cm). The pellet was put inside the cell which allowed to perform experiments under dynamical vacuum (10^{-6} hPa) or controlled atmosphere at various temperatures (between 300 and 870 K). The in-situ cell and the activation process have already been described in a previous paper.[11]

In all experiments, the samples were exposed for 1 h to methanol vapor (pressure 5 hPa). In order to remove the methanol atmosphere, the system was pumped under dynamical vacuum at different temperatures. The spectra of all samples were recorded at room temperature (RT) using a Nicolet FT-IR spectrometer in the 4000–400 cm^{-1} range with a 4 cm^{-1} resolution.

3 Results and Discussion

Both raw and chlorinated aluminas have already been the subject of a previous publication[11] in which the reactivity of the surface OH's with respect to chlorination has been studied. The infrared spectra recorded at different temperatures under evacuation after contact with methanol vapor are presented in Figs 1 and 2. The methoxylation of the raw surfaces was observed as predicted.[6,10] The methoxy groups were characterized by the symmetric $\nu_{(CH_3)}$ stretching mode; the splitting was due to the Fermi resonance with a symmetric deformation.[10] Their positions at room temperature are reported in Table 1. Moreover a broad absorption appeared at lower frequencies around 3200 cm^{-1}, more intense for Degussa alumina, associated with OH's linked by hydrogen bond.[11]

Besides these bands, the $\delta_{(CH_3)}$ deformation bands at 1474 and 1420 cm^{-1} and the $r_{(CH_3)}$ rocking band at 1190 cm^{-1} were identified. The $\nu_{(CO)}$ band for free CH_3OH was expected near 1030 cm^{-1};[12]

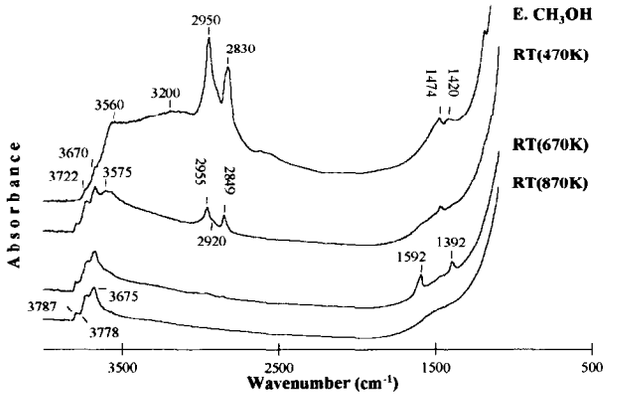

Fig. 1. FT-IR spectra of Degussa Al_2O_3 after adsorption of CH_3OH, after evacuation and after thermal treatment at 470, 670 and 870 K.

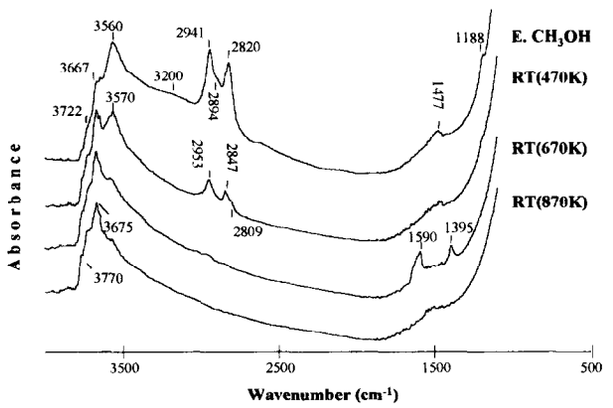

Fig. 2. FT-IR spectra of Condea Al_2O_3 after adsorption of CH_3OH, after evacuation and after thermal treatment at 470, 670 and 870°K.

the difference (Fig. 3) between the spectra of the activated, methoxylated alumina and that of the activated one showed a rather broad band located at 1110 and at 1098 cm^{-1} for the Condea alumina and the Degussa one, respectively, which was a characteristic of methoxy groups.[13] The 12 cm^{-1} difference of $\nu_{(CO)}$ frequencies was related to the difference of $\nu_{(CH)}$ frequencies between Degussa and Condea alumina. This result might suggest that the chloride, introduced by the synthesis of Degussa alumina, could be in the network below the surface and could lead to an inductor effect.

The surface species, noted I, were assigned[14,15] to the adsorption of CH_3OH at octahedral (hexacoordinated) aluminium sites through the oxygen atom. Its formation was connected with the

Table 1. Frequencies of $\nu_{(CH_3)}$ (cm^{-1}) for the raw and Cl-treated aluminas

	Degussa Al_2O_3		*Condea Al_2O_3*	
Surface species	*I*	*II*	*I*	*II*
$+CH_3OH$	2950 2830	2955 2849	2941 2820	2953 2847
Treated by $HCl+CH_3OH$	2957 2843	2961 2853	2955 2831	2960 2850
Treated by $CHCl_3+CH_3OH$	2960 2841	2978 2851	2960 2828	2972 2852

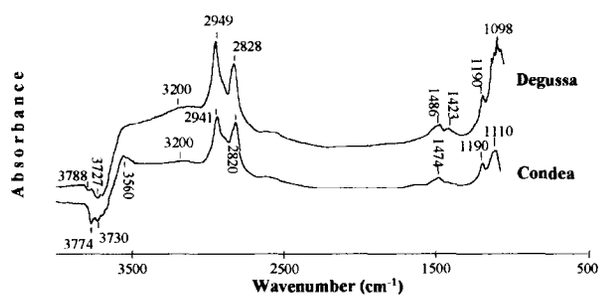

Fig. 3. Difference spectra of Degussa Al_2O_3 and Condea Al_2O_3 (after evacuation of CH_3OH–after activation of Al_2O_3).

disappearance of OH bands (Fig. 3) according to the scheme:

$$Al - OH + CH_3OH \rightarrow Al - OCH_3 + H_2O$$

By outgassing at increasing temperatures up to 870 K, we observed both a progressive intensity decrease of CH stretching bands and a shift of the $\nu_{(CH)}$ positions towards higher wavenumbers. These $\nu_{(CH)}$ frequencies (Table 1) belonged to another species, noted II, usually assigned to adsorption of CH_3OH on tetrahedral aluminium sites.[14] It could be noticed that, whereas the $\nu_{(CH)}$ frequencies of methanol adsorbed on tetrahedral sites (species II) were practically identical, those of methanol adsorbed on the octahedral ones (species I) indicated a much stronger effect for the Condea alumina. The octahedral sites of Condea alumina behaved therefore as stronger electron acceptors with respect to those of Degussa alumina.

Above 470 K, the methoxy species tended to disappear and a new species appeared, identified as formate groups associated with bands at 1592 cm^{-1} [$\nu_{(COO)}$] and 1392 cm^{-1} [$\delta_{(CH)}$]. The $\nu_{(CH)}$ frequency was very weak but could be located at 2920 cm^{-1}. Surface methoxy groups can indeed be oxidized on the surface[16] through step-wise hydrogen losses producing surface bound species such as formaldehyde with the final formation of formate. The intensity of the 1592 cm^{-1} [$\nu_{(COO)}$] band depended on the temperature and showed a maximum at 670 K (Table 2). Above 670 K, formate ions could be easily decomposed over metal oxides into CO and OH^-.[10,14] What is not definitely established is how formate ions are formed from methanol over a non transition non-oxidizing metal oxide catalyst like alumina. A plausible answer to this question has been given in a study on formaldehyde adsorbed on alumina.[17]

The adsorption of CH_3OH on the alumina surfaces chlorinated both by HCl and $CHCl_3$ showed (Figs 4–7) two bands including both I and II species with a similar intensity. The frequencies are reported in Table 1. In the range below 1500 cm^{-1}, $\delta_{(CH)_3}$ and $r_{(CH)_3}$ bands were again observed. The formation of hydrogen bonded OH groups (3200 cm^{-1}) was more pronounced on the treated Degussa sample than on the treated Condea one: in both cases the band intensity decreased with thermal treatment. We can observe from Table 1 that, in all cases, the CH frequencies of methanol adsorbed on chlorinated surfaces were less down-shifted than

Table 2. Integrated intensities (A) of formate $\nu_{(COO)}$ (1592 cm^{-1}) band measured at several temperatures for raw and treated by HCl aluminas

	Condea Al_2O_3		*Degussa Al_2O_3*	
T (K)	*Raw*	*Treated by HCl*	*Raw*	*Treated by HCl*
	A	A	A	A
370	/	/	0	0·5
470	0·5	0·9	0	1·2
570	1·9	1·6	3·6	1·4
670	11·3	10	6·2	2·7
770	2·4	4	1	1·7
870	0·2	0·7	0	0·6

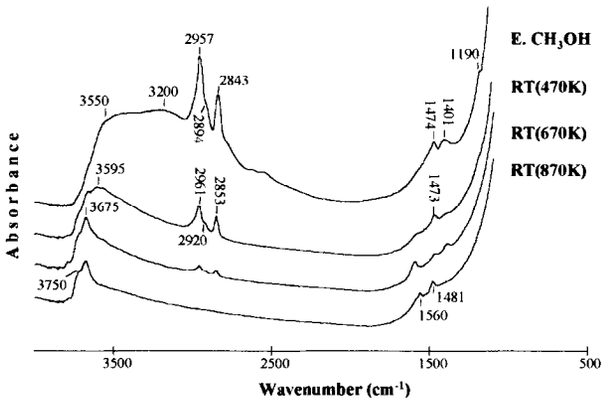

Fig. 4. FT-IR spectra of Degussa Al_2O_3 after treatment with HCl and adsorption of CH_3OH, after evacuation and after thermal treatment at 470, 670 and 870 K.

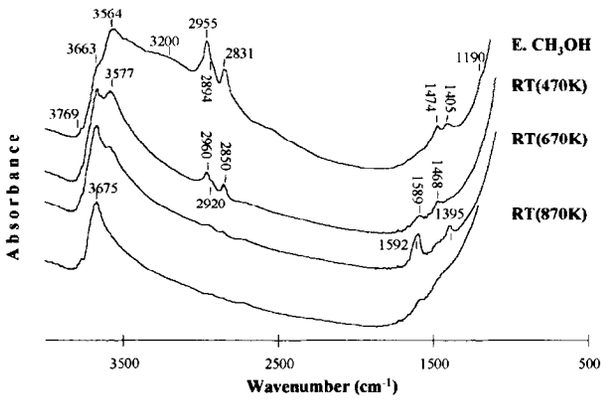

Fig. 5. FT-IR spectra of Condea Al_2O_3 after treatment with HCl and adsorption of CH_3OH, after evacuation and after thermal treatment at 470, 670 and 870 K.

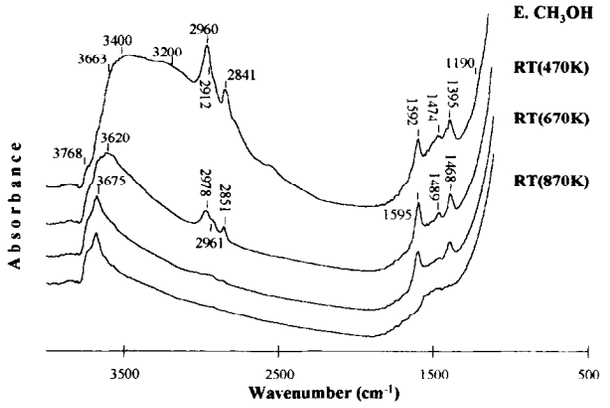

Fig. 6. FT-IR spectra of Degussa Al_2O_3 after treatment with $CHCl_3$ and adsorption of CH_3OH, after evacuation and after thermal treatment at 470, 670 and 870 K.

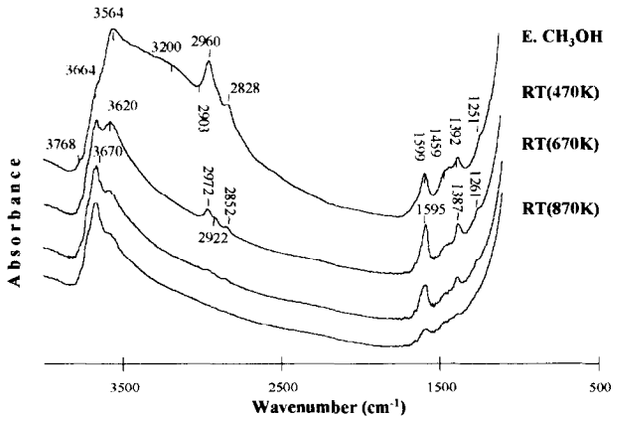

Fig. 7. FT-IR spectra of Condea Al_2O_3 after treatment with $CHCl_3$ and adsorption of CH_3OH, after evacuation and after thermal treatment at 470, 670 and 870 K.

those of the same molecule adsorbed on the raw aluminas with respect to the value of the free molecule (2971, 2844 cm^{-1}).[12] The effect could be due to a direct interaction between methyl hydrogen atoms and surface hydroxyl or chloride atoms since the $\nu_{(CO)}$ frequencies, in the 1100 cm^{-1} region, of both raw and treated aluminas were identical [Fig. 8(a) and (b)]; this effect is different from that observed before chlorination. The $\nu_{(CO)}$ frequencies depend on the nature of the initial compound.

The formation of formates on the surface chlorinated by HCl was evidenced from 470 K by bands at 2920, 1592 and 1393 cm-1 similar to those of the raw alumina. The variation of the integrated intensities of the 1592 cm^{-1} band (A) with temperature (Table 2) showed the same feature as for the raw sample; a maximum of intensity was reached at 670 K. At the end of the thermal

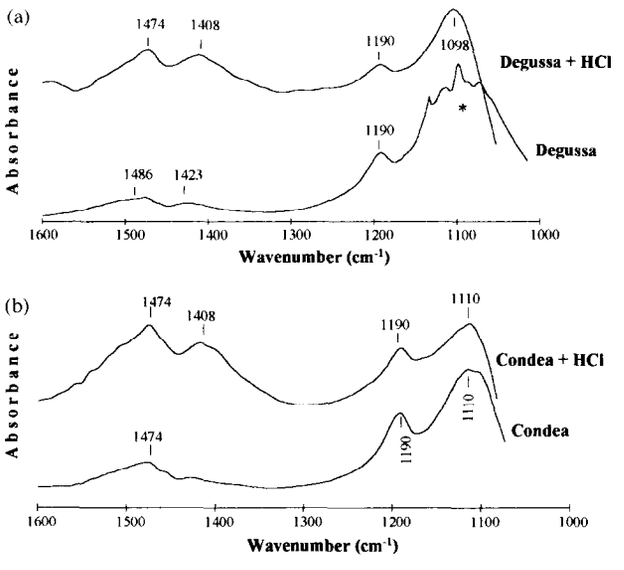

Fig. 8. Difference spectra of (a) Degussa Al_2O_3, (b) Condea Al_2O_3 treated by HCl (after evacuation of CH_3OH–after activation of Al_2O_3). *These lines are due to water vapor.

Table 3. Integrated intensities (A) of formate $\nu_{(COO)}$ (1592 cm^{-1}) and measured at several temperatures for Condea and Degussa alumina treated by $CHCl_3$

	$CHCl_3$ treatment	
T (K)	*Condea*	*Degussa*
	A	A
370	12·3	9·4
470	12·2	9·3
570	12·4	9
670	**8·8**	**8**
770	5·4	4·1
870	3·1	1·7

treatment (870 K), formate bands disappeared. In the case of the aluminas treated with $CHCl_3$ and then thermally treated, formate bands were already visible at the evacuation of CH_3OH. These bands still existed at the higher temperatures (Table 3). The decrease of the values of the integrated intensities with increasing temperature was probably due to two opposite effects: a decrease of formate due to the decomposition of $CHCl_3$[11] and an increase of their formation from CH_3OH. Even at the end of the treatment, a small amount of formate was still present.

Only for the Degussa sample, were noted both the presence of the two bands at 1560 and 1481 cm^{-1} corresponding to a different surface species and the absence of bands in the range of $\nu_{(CH)}$ at 2922 cm^{-1} (Fig. 4). These bands could be assigned to acetates whose $\nu_{(CH)}$ intensities were expected to be very weak. The action of CH_3COOH on Degussa Al_2O_3 led to the same couple of bands and the thermal treatment of alumina surfaces exposed to HCOOH showed the same result which could derive from the interaction of the nucleophilic oxygen of CH_3OH with the electrophilic carbon of adsorbed formate according to the scheme proposed in Fig. 7 of Domokos *et al.*[16] .

It can be concluded that the chlorination modifies the surface behaviour of both Degussa and Condea aluminas with respect to methanol adsorption as evidenced from the shifts of its $\nu_{(CH)}$ frequencies and from a modification of its chemical evolution into formate.

Acknowledgements

Financial support from CNR (Short-term mobility program) to one of us (V.L) is gratefully acknowledged. This work was partly supported by the Conseil Régional du Limousin.

References

1. Rossi, R. F., Bassolo, M., Oliveri, G. and Guzzo, F., Heat of chemisorption of 1-propanol on a-Al_2O_3 at 25–200°C. A microcalorimetric study. *Journal of Therm. Analys.*, 1994, **41**, 1227–1237.
2. Rossi, P. F., Oliveri, G. and Guzzo, F., Variation of the chemisorption of methanol on a-Al_2O_3 in the range of 200–300°C. *Thermochimica Acta*, 1993, **227**, 59–66.
3. Lu, M., Zhao, G. X. H., Cui, W., Gu, J. and Bauser, H., Dehydratation of 1-butanol over γ-Al_2O_3 catalytic membrane. *Catal. Today*, 1995, **25**, 339–344.
4. de Miguel, S. R., Martinez, A. C., Castro, A. A. and Scelza, O. A., Effect of lithium addition upon γ-Al_2O_3 for isopropanol dehydration. *Journal of Chem. Tech. Biotechnol.*, 1996, **65**, 131–136.
5. Ko, A. N., Yang, C. L., Zhu, W. and Lin, H., Selective N alkylation of aniline with methanol over γ-alumina. *Appl. Catal. A*, 1996, **134**, 53–66.
6. Greenler, R. G., Infrared study of the adsorption of methanol and ethanol on aluminum oxide. *Journal of Chem. Phys.*, 1962, **37**, 2094–2100.
7. Deo, A. V. and Dalla Lama, I. G., An infrared study of the adsorption and mechanism of surface reactions of: 1—Propanol on γ-alumina and γ-alumina doped with sodium, hydroxide and chromium oxide. *Journal of Phys. Chem.*, 1969, **73**, 616–623.
8. Kagel, R. O., Infrared investigation of the adsorption and surface reactions of the C through C_4 normal alcohols on γ-alumina. *Journal of Phys. Chem.*, 1967, **71**, 844–850.
9. Lamotte, J., Saur, O., Lavalley, J. C., Busca, G., Rossi, P. F. and Lorenzelli, V., Coadsorption of methanol and carbon dioxide on alumina. *Journal of Chem. Soc. Faraday Trans.*, 1986, **82**, 3019–3023.
10. Busca, G., Infrared studies of the reactive adsorption of organic molecules over metal oxides and of the mechanisms of their heterogeneously-catalyzed oxidation. *Catal. Today*, 1996, **27**, 457–496.
11. H. Vigué, Quintard, P., Merle-Méjean and Lorenzelli, V., An FT-IR study of the chlorination of γ-alumina surfaces. *Journal of European Ceramic Society*, 1998, **18**, 305–309.
12. Herzberg, G., *Molecular Spectra and Molecular Structure, II—Infrared and Raman Spectra*, ed. D. Van Nostrand, Princeton, New Jersey, 1945.
13. Lamotte, J., Moravek, V., Bensitel, M. and Lavalley, J. C., FT-IR study of the structure and reactivity of methoxy species on thorium dioxide and ceria. *React Kinet. Catal. Lett.*, 1988, **36**, 113–118.
14. Busca, G., Rossi, P. F., Lorenzelli, V., Benaissa, M., Travert, J. and Lavalley, J. C., Microcalorimetric and Fourier transform infrared spectroscopic studies of methanol adsorption on Al_2O_3. *Journal of Phys. Chem.*, 1985, **89**, 5433–5439.
15. Luck, W. A. P. and Fritzsche, M., The OH stretching mode and a three species model of liquid methanol. *Z. Phys. Chem.*, 1995, **191**, 71–86.
16. Domokos, L., Katona, T. and Molnàr, A., Dehydrogenation of methanol to methyl formate: deuterium labeling studies. *Catal. Lett.*, 1996, **40**, 215–221.
17. Busca, G., Lamotte, J., Lavalley, J. C. and Lorenzelli, V., FT-IR study of the adsorption and transformation of formaldehyde on oxide substrates. *Journal of Am. Chem. Soc.*, 1987, **109**, 5197–5202.