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Chlorination of alumina: an IR spectroscopic study

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Summary — Chlorination of γ-alumina with various reagents (tetrachloromethane, hexachloroethane, hexachloropropanone, thionyl chloride and hydrogen chloride) was followed by IR analysis of the gaseous products. CCl_4 and $SOCl_2$ directly react with the surface at 550 K. Chlorination with C_2Cl_6 occurs at 650 K, together with decomposition into Cl_2 and C_2Cl_4. Reaction with C_3Cl_6O first involves a decomposition yielding $COCl_2$ and C_2Cl_6, which then react with alumina. In any case, chlorination converts the surface hydroxyl groups as well as some oxide ions. The surface acidity of the various Al_2O_3/Cl samples was then studied by infrared spectroscopy of adsorbed basic molecules. Whatever the chlorination procedure, pyridine detected Lewis acid centers of comparable strength and density. In addition, pyridinium ions appeared on alumina samples chlorinated with HCl, but the corresponding Brönsted acidity could no longer be evidenced when the solids were outgassed above 370 K prior to pyridine adsorption. Similarly, lutidine detected Lewis centers and the various samples could be ranked in order of their acidic strength. Moreover, lutidinium ions were found on most samples, and vanished at 420 K. Thus, the occurrence of Brönsted sites is ascribed to some weakly bound HCl. The surface acidity is presumably very strong, as the solids catalyze the alkylation of isobutane with ethylene. Spectroscopic and catalytic data were compared and the selectivity for monoalkylation (versus, for example, multiple alkylation) appears to correlate with the number of Brönsted sites.

chlorinated alumina / chlorine compound / IR spectroscopy / acidity / pyridine / lutidine

Résumé — Chloration de l'alumine : étude par spectroscopie IR. La chloration de l'alumine γ par différents réactifs (tétrachlorométhane, hexachloroéthane, hexachloropropanone, chlorure de thionyle et chlorure d'hydrogène) a été suivie en analysant les produits gazeux par spectroscopie infrarouge. CCl_4 et $SOCl_2$ réagissent directement avec la surface à 550 K. La chloration par C_2Cl_6 intervient à 650 K, en même temps que sa décomposition en Cl_2 et C_2Cl_4. La réaction avec C_3Cl_6O implique d'abord une décomposition en $COCl_2$ et C_2Cl_6 qui réagissent avec l'alumine. Dans chaque cas, la chloration transforme les groupements hydroxyles de surface ainsi que certains ponts oxygène. L'acidité de surface des diverses alumines chlorées a alors été étudiée par spectroscopie infrarouge de molécules basiques adsorbées. Quel que soit le mode de chloration, la pyridine détecte des sites d'acides de Lewis de force et de densité comparables. De plus, des ions pyridinium apparaissent sur les alumines chlorées par HCl, mais l'acidité de Brönsted correspondante n'est plus détectée si l'on dégaze les solides au-delà de 370 K avant d'adsorber la pyridine. De même, la lutidine détecte des sites de Lewis et les différents échantillons ont pu être classés selon leur force acide. Des ions lutidinium sont aussi détectés sur la plupart des échantillons, mais ils disparaissent à 420 K. Par conséquent, la présence de sites de Brönsted est attribuée à du HCl faiblement lié. L'acidité de surface est probablement très forte, car les solides catalysent l'alkylation de l'isobutane par l'éthylène. Les données spectroscopiques et catalytiques ont été comparées : la sélectivité en monoalkylation (opposée par exemple à l'alkylation multiple) semble en accord avec le nombre de sites de Brönsted.

alumine chlorée / composé chloré / spectroscopie infrarouge / acidité / pyridine / lutidine

Introduction

Chlorinated alumina is a solid catalyst that exhibits high surface acidity. For instance, the refining industry employs Al_2O_3-Cl catalysts to isomerize n-alkanes at moderate temperature [1, 2]. Other possible catalytic applications include polymerization of C_3-C_6 alkenes [3], cracking of long chain alkanes [4], alkylation of isobutane by ethylene [5] or destruction of chloroalkanes [6].

The most active Al_2O_3-Cl catalysts contain a minimum of 5% chlorine by weight. Starting with alumina dehydrated at about 700 K, the chlorinated solids may be obtained in a number of ways.

One method involves the grafting of $AlCl_n$ entities onto superficial Al-OH groups. This may be achieved through interaction of alumina with aluminum chloride at 400–600 K [7] or, better, with the dimeric compound $(C_2H_5)_3Al_2Cl_3$ at 520 K [8].

A second method involves the reaction of alumina with gaseous compounds such as gem-dichloro derivatives of methane [1] or thionyl chloride [9]. Upon reaction with tetrachloromethane at 500 K, surface hydroxyl

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Table I. Nomenclature and preparation of the Al_2O_3-Cl samples.

Symbol	*Activation (T/K)*	*Reagent*	*Reaction (T/K)*	*Initial pressure (Pa)*	*Cl level (wt.%)*
G-1a	670	CCl_4	550	2 000	4.3
G-1b	1050	CCl_4	550	2 000	3.2
G-2	670	C_2Cl_6	650	25	4.7
G-3	670	C_3Cl_6O	550	25	5.7
G-4	670	$SOCl_2$	550	2 100	3.8
P-1	670	HCl	550	2 000	2.4
P-2	670	HCl	700	2 000	2.9
P-3	940	HCl	940	16 000	2.5
P-4	670	HCl	920	16 000	2.8
P-5	670	HCl	670	16 000	3.1
PH-1	940	$HCl+H_2$	940	13 000:3 000	1.9
S-1	670	CCl_4 then	550	2 000	
		$HCl + H_2$	550	12 000:3 400	2.4

groups are substituted by chlorine atoms and some oxide ions are replaced by two Cl atoms. Above 570 K, nascent aluminum chloride is formed, and grafting as $>$Al-O-$AlCl_2$ has been suggested by Primet [10].

A third method consists of reacting alumina with hydrogen chloride. At room temperature HCl is dissociatively adsorbed on alumina [11, 12] but the catalytic activity remains low. Kytökivi [13] studied the reaction with HCl at temperatures up to 870 K. Catalysts prepared at such high temperatures are very active in alkane isomerization [14]. Thus, whenever the catalytic reaction is very demanding, retention of HCl on the solid appears necessary [15]. Accordingly, HCl may be adsorbed to some extent over an alumina sample previously chlorinated by CCl_4 [16] and surface complexes such as O-$AlCl_2$·HCl have been postulated.

Several authors have used the infrared spectra of adsorbed pyridine to probe the acidity of such solids. They generally conclude that coordination of pyridine on Lewis acid sites of Al_2O_3-Cl is stronger than over dehydrated alumina, due to electron depletion induced by chloride ions [10]. Furthermore, some pyridinium ions were detected upon adsorption of pyridine on a CCl_4-treated alumina which was then in contact with HCl at 570 K [16], but the intensity of the pyridinium bands strongly decreased when the solid was placed under vacuum at 420 K before pyridine adsorption. Authors concluded that the hydrogen chloride adduct on the chlorinated surface was rather unstable.

The acidity of Al_2O_3-Cl therefore depends to a large extent on the chlorination procedure. The present study compares the features of the reaction between alumina and the following compounds: tetrachloromethane (CCl_4), hexachloroethane (C_2Cl_6), hexachloropropanone (C_3Cl_6O), thionyl chloride ($SOCl_2$) and hydrogen chloride. The chlorination was performed in an isothermal closed vessel, part of which was an infrared cell. Thus, gaseous reaction products were determined by infrared spectroscopy. The different Al_2O_3-Cl samples obtained in this way were previously tested as catalyst for the alkylation of isobutane by ethylene at 270–320 K [17]. Accordingly, the acidic properties of these catalysts were checked through IR monitored adsorption of the bases pyridine and 2,6-dimethylpyridine (lutidine).

Experimental section

Material and reagents

The starting material was a commercial γ-alumina (Ketjen CK 300) under the form of extrudates. The solid was poorly crystallized, only the γ-phase was detected by X-ray diffraction. BET surface area was 180 m^2g^{-1} and reported impurities were SiO_2 (90 ppm), Fe_2O_3 (100 ppm) and Na_2O (10 ppm). Extrudates were ground to a grain size under 400 mesh and then this powder was pressed into self-supporting thin wafers, 20 mg in weight, for the purpose of IR studies.

The reagents CCl_4 (Aldrich), $SOCl_2$ (Prolabo) and C_3Cl_6O (Janssen) were distilled before use. The solid C_2Cl_6 (Janssen) was 99% grade. Pyridine and 2,6-dimethylpyridine (Merck) were stored over 3 Å zeolite. The HCl gas was taken from a cylinder (Union Carbide, technical).

Chlorination procedure

Chlorination was performed in a wide-bore quartz tube, 375 mL in volume, which could be connected to a vacuum facility incorporating gas entries. The lower end of the tube terminated in an IR cell fitted with KBr windows.

The alumina wafer positioned in the upper section was heated at 670 K, first in oxygen, then under vacuum, in order to achieve a standard hydroxyl content. The temperature was then adjusted for chlorination and the vaporized reagent, which had been purified by freeze-pump-thaw cycles, was introduced in the vessel. The initial pressure depended on the particular compound. With a given alumina wafer, several reactions, 30 min each, had to be performed successively with renewed atmosphere in order to fix a minimum of 3% chlorine on the solid. After the last dose had reacted, the temperature was raised by 25 K for the final pumping. When chlorination was performed with HCl or a ($HCl + H_2$) mixture, the gas phase was maintained while cooling the chlorinated solid down to temperature T_{ev} (generally 370 K) for the final pumping.

The final chlorine contents (wt%) were determined by microanalytical combustion followed by argentimetry (CNRS, Solaize). The Al_2O_3-Cl samples obtained in this way are listed in table I.

Table II. Gas phase vibrational frequencies (cm^{-1}) in the region 500–1800 cm^{-1}.

Compound	*Reference [18]*	*Other*	*This work*
CCl_4	1550, 1250, 1220, 1000, 970, 780	785, 762, 754 [19]	1559, 1257, *1008*, 779
C_2Cl_6	780, 680	769, 675 [20]^b	*791*, 685, 669
C_2Cl_4	900, 800, 780, 750	913, 802, 782 [21]	*916*, 802, 782
$COCl_2$		1827^a, 849^a [22]	*1834*, *1819*, *852*
C_3Cl_6O	1780, 1750, 1100, 893, 840		1103, *898*, *850*
$SOCl_2$		1253^a, 950, 492, 455 [23]	*1256*, *1245*, 502, 492, 464, 457
SO_2		1360, 1152^a, 518^a [24]	*1360*, 1165, 1136, 533, 505

[a] Fundamental vibrations with a (P, Q , R) structure. [b] Solution in CCl_4.

IR spectroscopy

IR transmission spectra were recorded through the cell (pathlength 5 cm) by means of a Nicolet 710 FTIR instrument operated at a resolution of 4 cm^{-1}. During the chlorination step, IR spectra were recorded through the gas in order to identify the volatile products. Band assignments are reported in table II. The intensities of the italic-typed bands were used to estimate the relative amounts of particular compounds. Water and carbon dioxide could not be determined in this way, due to a residual signal in the apparatus.

After chlorination, the pellet was shifted down to the IR cell for inspection of the solid and adsorption experiments. Gaseous pyridine and lutidine were in contact with the sample at room temperature under 130 Pa pressure. The sample was then evacuated at 300 K or (after moving) at 420 K and IR spectra were recorded at the beam temperature.

Reaction between alumina and the various reagents

The conditions of the reaction between alumina and the various reagents appear in table I. In order to fix 3–5% Cl, the temperature was set at 550 K for CCl_4 (samples G-1a and G-1b), C_3Cl_6O (G-3) and $SOCl_2$ (G-4) and at 650 K for C_2Cl_6 (sample G-2). HCl reacted at several temperatures between 550 and 940 K (samples P-1 to P-5 and PH-1).

Tetrachloromethane

The initial pressure of tetrachloromethane was 2000 Pa, so that every dose contained 20 times the amount necessary to fix 5% Cl on alumina. The IR spectrum recorded immediately after the first introduction already contained the bands of phosgene ($COCl_2$) and hydrogen chloride. Later on, these bands increased slowly, whereas those due to CCl_4 decreased very little. Although the consumption of CCl_4 could not be determined, the initial appearance of HCl denotes a very fast reaction with the surface hydroxyls. Regardless of the site structure, this may be written as follows:

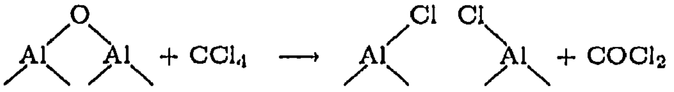
$$>\mathrm{Al\text{-}OH} + \mathrm{CCl_4} \rightarrow\ >\mathrm{Al\text{-}Cl} + \mathrm{COCl_2} + \mathrm{HCl}$$

Although $COCl_2$ itself has been shown to react with the solid [25, 26]:

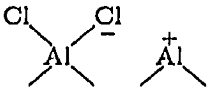
$$>\mathrm{Al\text{-}OH} + \mathrm{COCl_2} \rightarrow\ >\mathrm{Al\text{-}Cl} + \mathrm{CO_2} + \mathrm{HCl}$$

there was no tendency for the $COCl_2$ bands to go through a maximum in the course of a run. Indeed, such a reaction appeared very slow under our conditions.

When the gas present after 30 min reaction was pumped out, a second dose of CCl_4 reacted to some extent. At the end of this second run, the amount of $COCl_2$ was 37% of that found previously and that of HCl 1.5% only. Thus, concurrently with the substitution of hydroxyls, some of the oxide ions were attacked:



The above equation does not infer any particular structure for the acidic site which might well be pictured as [1]:



The exchange of one surface oxygen with two chlorine atoms was previously mentioned by Basset [27] for the reaction with CCl_4 above 670 K. Interestingly, the same stoichiometry was verified by Reti in the reaction with elemental chlorine [28]. As proposed by Bond [29] the O-Cl substitution may proceed stepwise: the chlorinated reactant is first disrupted at a Lewis acid site of alumina with formation of transient species such as $AlCl_2$ and $AlCl_3$ which react further. The action of CCl_4 depends somewhat on the temperature of alumina pretreatment. When alumina was activated at 1050 K instead of 670 K, thus bearing fewer OH groups, then chlorination with CCl_4 released very little HCl. The amount of $COCl_2$ was also lower, nevertheless the final Cl level was significant: 3.2% in sample G-1b (table I). Therefore the oxide bridges are able to react even though the surface is devoid of OH groups.

Thionyl chloride

Thionyl chloride is less stable than tetrachloromethane and, in the absence of alumina, a limited decomposition to sulfur dioxide and hydrogen chloride was observed at 300 K. This may be due to the residual water present in the reactor.

When alumina was allowed to react at 550 K with a large excess of $SOCl_2$, 32% of the first dose of thionyl chloride disappeared within 30 min, while SO_2 and

HCl were produced. Subsequent doses of $SOCl_2$ reacted to a much smaller extent. Again, SO_2 and HCl were detected. Analysis of sample G-4 revealed a Cl content of 3.8% with only 0.6% sulfur. Thus, $SOCl_2$ mainly led to fixation of chlorine and we may write the reaction as:

$$\rangle\text{Al-OH} + SOCl_2 \longrightarrow \rangle\text{Al-Cl} + SO_2 + HCl$$

and
$$\rangle\text{Al-O-Al}\langle + SOCl_2 \longrightarrow 2\ \rangle\text{Al-Cl} + SO_2$$

Besides, a sizeable fraction of $SOCl_2$ probably underwent decomposition into SO_2, Cl_2 and other products. Among these, disulfur dichloride (S_2Cl_2) was not clearly identified. Such a decomposition may account for the relatively small amount of Cl fixed on alumina (table I).

Hexachloroethane

With this compound and the following, the amount of chlorine in one dose was only 1% the weight of alumina, and up to ten doses were reacted successively with the same wafer. However, hexachloroethane appeared far less reactive than tetrachloromethane, so that the chlorination was performed at 650 K for sample G-2.

Under these conditions, the formation of carbon monoxide and hydrogen chloride was evident through their characteristic vibration-rotation bands. The bands of $COCl_2$ were notably absent, whereas additional bands appeared at 782, 802 and 916 cm^{-1} (fig 1) denoting the formation of tetrachloroethylene. In figure 2, the band intensities are plotted as a function of time for the various compounds; an arbitrary scale is used for each band, so that figures are not to be compared from compound to compound. Upon introducing the first dose, 90% of C_2Cl_6 reacted within 30 min, whereas C_2Cl_4, HCl and CO steadily increased. When successive doses of C_2Cl_6 were introduced, the distribution of the reaction products changed somewhat: the ninth exposure for instance produced much C_2Cl_4 but little HCl and no CO.

Thus, the reaction of C_2Cl_6 with alumina is mainly:

$$C_2Cl_6 + 2\ \rangle\text{Al-OH} \longrightarrow 2\ \rangle\text{Al-Cl} + 2\,CO + 2\,HCl + Cl_2$$

and
$$C_2Cl_6 + 2\ \rangle\text{Al-O-Al}\langle \longrightarrow 4\ \rangle\text{Al-Cl} + 2\,CO + Cl_2$$

As the CO/HCl ratio decreased with number of doses, the reactivities of the hydroxyl groups and of the oxide ions towards C_2Cl_6 are not so different. Besides, hexachloroethane is thermally unstable and undergoes a reversible decomposition

$$C_2Cl_6 \rightleftharpoons C_2Cl_4 + Cl_2$$

This decomposition is catalyzed by the solid, and tends to become the major pathway as chlorination proceeds. Sample G-2 was found to contain 4.7% Cl and about 2% carbon; the latter probably arises from complete degradation of C_2Cl_4. Similar high carbon contents have been found when reacting alumina with chloroalkenes, or molecules which easily decompose into them [6, 26].

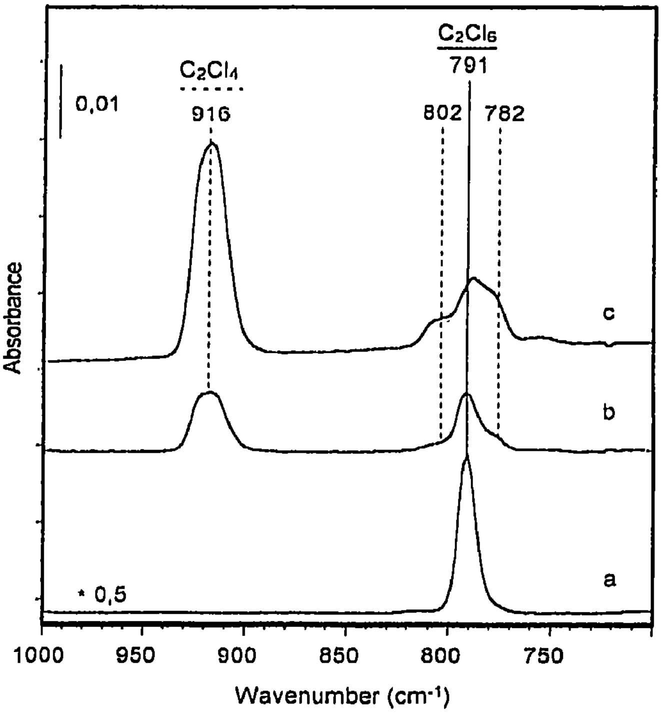


Fig 1. Reaction of C_2Cl_6 with alumina at T = 650 K. Infrared spectra (region 700–1000 cm^{-1}) recorded through the gas phase: a) pure C_2Cl_6; b) after 30 min contact with the first dose of C_2Cl_6; c) after 30 min contact with the tenth dose of C_2Cl_6.

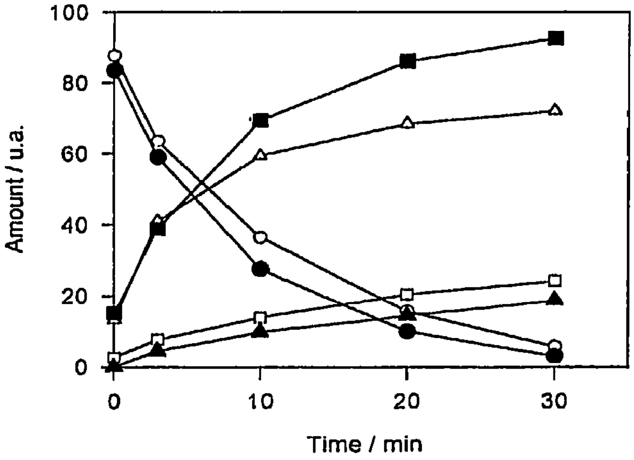


Fig 2. Reaction of C_2Cl_6 with alumina at T = 650 K: variation of the relative amounts (ua) of compounds with time. Run 1: C_2Cl_6 ●; C_2Cl_4 ▲; HCl ■. Run 9: C_2Cl_6 ○; C_2Cl_4 △; HCl □.

Hexachloropropanone

In spite of its low volatility, hexachloropropanone was more reactive than hexachloroethane, allowing chlorination of alumina at 550 K (sample G-3 in table I). Upon introducing the first dose, the IR bands at 850 and 898 cm^{-1} characteristic of C_3Cl_6O decreased immediately and fell to zero within 10 min. A number of new bands appeared, indicating the formation of hydrogen chloride, carbon monoxide, phosgene, hexachloroethane and tetrachloroethylene. Figure 3 shows the bands characteristic of $COCl_2$, C_2Cl_6 and C_2Cl_4. (The region where the bands of CO and HCl appear is not shown.)

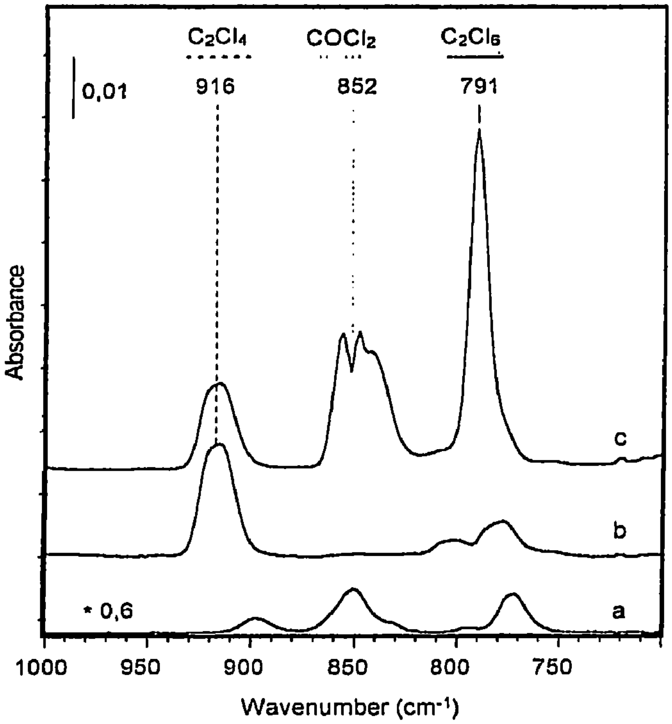


Fig 3. Reaction of C_3Cl_6O with alumina at $T = 550$ K. Infrared spectra (region 700–1000 cm^{-1}) recorded through the gas phase: a) pure C_3Cl_6O; b) after 10 min contact with the first dose of C_3Cl_6O; c) after 10 min contact with the tenth dose of C_3Cl_6O.

The amounts of the reagent and products varied with reaction time as shown in figure 4 for doses 1, 3, 6 and 14. In each run, CO and C_2Cl_4 appeared initially and grew on steadily. The final amount of CO recorded after 30 min slowly increased run after run, while that of C_2Cl_4 slightly decreased. Hydrogen chloride also appeared right at the start of the earlier runs, and then increased with time. Subsequent reactions gave much less HCl. $COCl_2$ and C_2Cl_6 were not detected when reacting doses 1 and 2. Starting at dose 3, they were both produced in increasing amounts. From then on, a maximum in $COCl_2$ was found after about 5 min reaction whereas C_2Cl_6 always increased. From the above results, it may be inferred that hexachloropropanone does not itself react with alumina. Reaction with the solid is preceded by decomposition along two routes:

$$C_3Cl_6O \longrightarrow CO + C_2Cl_6$$

$$C_3Cl_6O \longrightarrow COCl_2 + C_2Cl_4$$

C_2Cl_4 remains virtually unchanged, while $COCl_2$ and C_2Cl_6 both react with the surface hydroxyls and oxide ions of alumina until a 5.7% level is achieved. In this process, C_2Cl_6 is less efficient than $COCl_2$ since it appears first in the gas phase (fig 4).

Hydrogen chloride

Dehydrated alumina was reacted with successive doses of HCl (13 000 Pa) at various temperatures, and then cooled down to 370 K before evacuation, (samples P in table I). The IR spectra of the gas phase recorded during the reaction failed to indicate whether hydroxyls or oxide ions were attacked first, since the ratio between HCl consumed and water evolved could not be estimated. Alumina samples reacted at 550 K (P-1), 700 K (P-2) and 940 K (P-3), had final Cl contents of respectively 2.4 2.9 and 2.5%. Reaction with a (HCl + H_2) mixture led to a lower extent of chlorination: 1.9% at 940 K (sample PH-1). Possible changes in texture occurring upon high temperature chlorination were checked by nitrogen adsorption. Whereas heating alumina under N_2 at 940 K left the surface area unchanged at 180 m^2g^{-1}, chlorination at 940 K decreased the surface down to 150 m^2g^{-1}. The mean pore diameter determined according to reference [30] rose from 8 to 10 nm. Similar X-ray diffraction spectra were recorded for the starting material and for alumina heated or chlorinated at 940 K. Therefore, sintering occurred without appearance of a new alumina phase or improvement of crystallinity.

Finally, a sample chlorinated with CCl_4 at 550 K, ie, similar to G-1, was further treated with (HCl + H_2) at the same temperature (S-1 in table I). The final Cl content was lower than on G-1: 2.4% instead of 4.3%, but still higher than on samples reacted with HCl only.

IR study of the hydroxyls

Chlorination of alumina performed in a closed vessel is slightly less efficient than when using a gas flow [17]. With CCl_4, C_2Cl_6 and C_3Cl_6O the average chlorine level obtained here was only 5.2%, against 6% in the flow system. The difference was largest with $SOCl_2$ (3.2 vs 6%). For a solid with a surface area of 180 m^2g^{-1}, a 5% Cl content represents an average surface density of 4.7 Cl atoms per nm^2. This figure compares favorably with an estimated density of 5 OH groups nm^2 remaining after dehydroxylation at 670 K [31]. Since less and less HCl is released into the gas as the reaction proceeds, chlorination cannot be restricted to the hydroxyls and final Cl content should rather be compared with the density of Al exposed, ie, 8 Al atoms per nm^2 [31].

Accordingly, the IR spectra of the solids were recorded in the region 3200–3 900 cm^{-1} (fig 5). The unreacted γ-alumina (curve a) features three maxima at 3 675, 3 729 and 3 773 cm^{-1}, characteristic for three

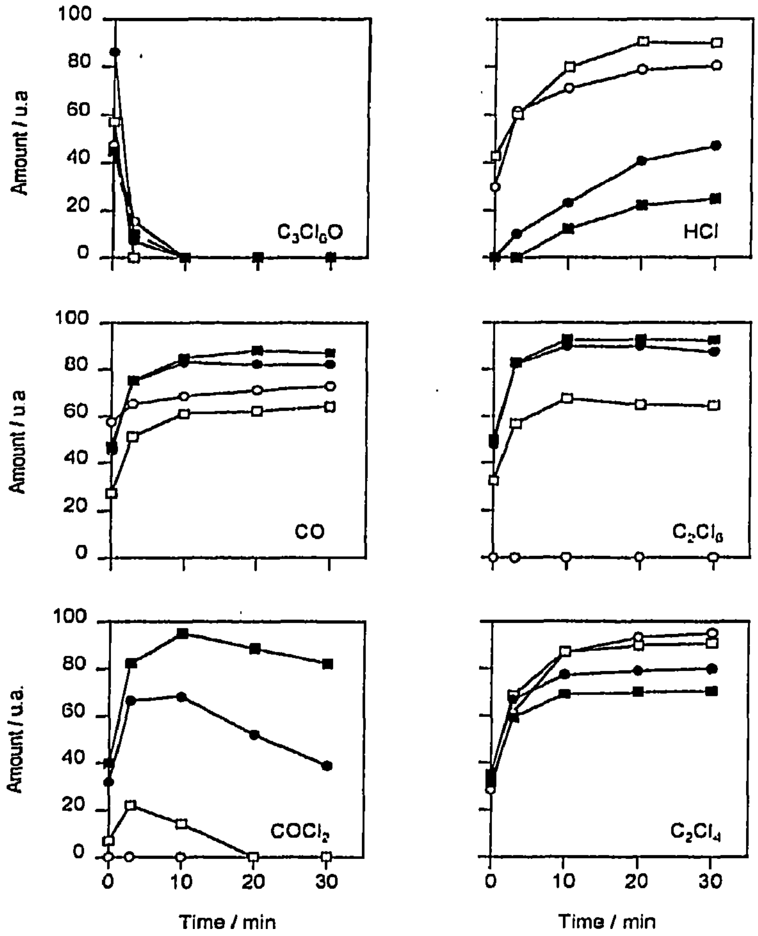


Fig 4. Reaction of C_3Cl_6O with alumina at T = 550 K: variation of the relative amounts (au) of C_3Cl_6O, HCl, CO, C_2Cl_6, $COCl_2$ and C_2Cl_4 along: ○ run 1; □ run 3; ● run 6; ■ run 14.

main types of OH groups. Such signals completely disappeared upon treatment with tetrachloromethane followed by evacuation at 575 K (curve **b**). With the other reagents, except HCl, the bands of free OH groups nearly disappeared, although they did not go strictly to zero. Thus the consumption of the hydroxyl groups is nearly quantitative and, at 550 K, hydrogen chloride is largely released from the surface. As seen before, each of the four G-reagents also reacted with some surface oxide ions, but at the temperatures investigated, the IR absorption of $AlCl_3$ at 1 380 cm^{-1} [32] was not detected.

The reaction between alumina and HCl or a (HCl + H_2) mixture was essentially different. As stated in the *Experimental section*, the reacted samples were cooled down under HCl before evacuation at moderate temperature. Curve d in figure 5 shows that after a reaction at 920 K followed by evacuation at 370 K, the absorption above 3 760 cm^{-1}, which is attributed to the more basic hydroxyls, completely disappeared, but OH bands were still detected at 3 673 and 3 728 cm^{-1}. An intense absorption appeared at lower wavenumber, with a broad maximum at 3 600 cm^{-1} corresponding to H-bonded hydroxyls. Indeed, the reaction with HCl produces water which is not fully released upon evacuation at 370 K, as shown by the persistence of a band at 1 630 cm^{-1}. Therefore, the H-bonded species responsible for the broad absorption may be H_2O as well as HCl. This agrees with the findings of Kitökivi et al [13] who concluded that a substitution of isolated hydroxyl groups for Cl with evolution of water and also dissociation of HCl on a Al-O site, leads to new hydroxyl groups which are more acidic than the original ones as they are in close proximity of a chlorine atom. According to these authors, the amount of HCl dissociated increases with decreasing reaction temperature.

A G-1 sample (chlorinated with CCl_4) was further contacted with HCl at 550 K, then cooled down to 370 K and evacuated. Spectrum c features a very broad absorption due to strongly perturbed OH vibrators. Thus, HCl reacts to some extent with the previously chlorinated surface, but the final state depends on the cooling and evacuation procedure.

Table III. Acidity of chlorinated alumina; IR features of pyridine species observed after evacuation at 300 K (pyridinium ions) and 420 K (coordinated pyridine).

Sample	*Chlorination reagent*[a] *T (K)*	T_{ev}[b] *(K)*	*Pyridinium* D_B *(μmol* g^{-1}*)*	*Coordinated on Lewis* $\bar{\nu}$ *19b* *(*cm^{-1}*)*	*Coordinated on Lewis* D_L *(μmol* g^{-1}*)*
CK-300	none	670	–	1623	130
G-1a	CCl_4/550	570	–	1626	220
G-1b	CCl_4/550	570	–	1624	150
G-2	C_2Cl_6/650	670	–	1626	260
G-3	C_3Cl_6O/550	570	–	1626	200
G-4	$SOCl_2$/550	570	–	1626	210
P-1	HCl/550	570	–	1624	210
P-2	HCl/700	700	–	1625	230
P-3	HCl/940	370	65	1626	180
P-4	HCl/920	370	35	1625	160
P-5	HCl/670	370	50	1625	160
S-2	CCl_4/550 then HCl + H_2/370	370	50	1624	110

[a] Alumina was evacuated at 670 K prior to chlorination, except G-1b (ev at 1050 K) and P-3 (ev at 940 K); [b] see *Experimental section*.

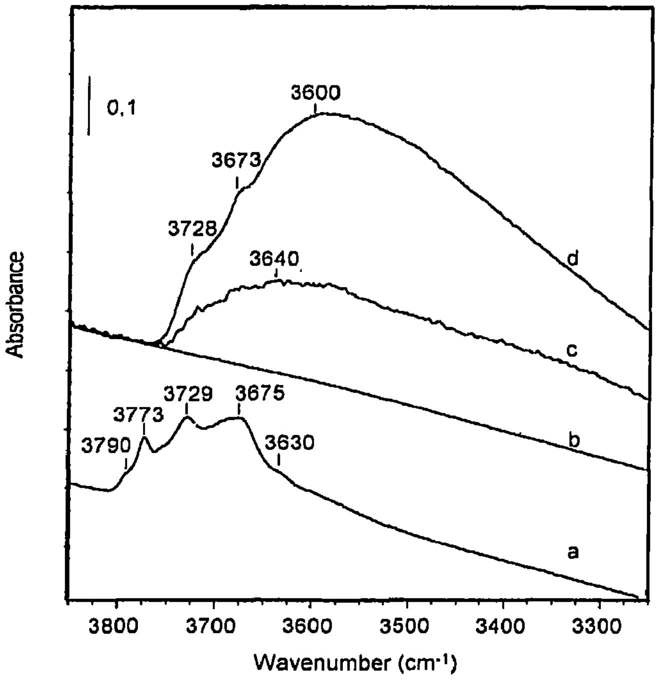


Fig 5. Infrared spectra of the solids in the 3 000–4 000 cm^{-1} region: a) γ-alumina dehydrated at 670 K; b) sample G-1 evacuated at 570 K; c) sample S-1 evacuated at 370 K; d) sample PH-1 evacuated at 370 K.

IR investigation of acidity

Adsorption of pyridine

Table III reports the main features of the spectra recorded of the various samples after contact with pyridine and mild evacuation. On γ-alumina, pyridine does not show any Brönsted sites, while IR bands appearing at 1 455 and 1 623 cm^{-1} belong to pyridine coordinated on Lewis centers. Such species are rather strongly bound since the bands remain intense after evacuation at 420 K.

With the chlorinated aluminas, all spectra recorded after pumping out the excess pyridine again display the signals of coordinated pyridine. The occurrence of pyridinium ions (PyH^+) was especially examined through the small band at 1540 cm^{-1}. This was completely absent for the G-n samples. On samples P-1 and P-2 which were reacted with HCl and then outgassed respectively at 570 and 700 K prior to pyridine adsorption, the PyH^+ bands could not be detected either. However, solids P-3, P-4 and P-5 which were cooled down under an HCl atmosphere and then evacuated at 370 K gave rise to PyH^+ formation, as well as solid S-2 which was treated with CCl_4 and HCl successively. Brönsted acidity is thus apparent on these solids, but all cationic species disappeared upon evacuating pyridine at 420 K. Therefore, the density of protonic sites (D_B μmol g^{-1}) was estimated from the intensity of the 1 540 cm^{-1} band remaining after evacuation at 300 K, using an integral molar extinction coefficient $\varepsilon = 1{,}67$ cm μmol^{-1} [33]. There are few such sites in any case, as the maximum amount is 65 μmol g^{-1} on solid P-3. Upon evacuating pyridine at 420 K, the L bands due to coordinated pyridine remained intense. The ν_{8a} vibration observed at 1623 cm^{-1} with pure alumina was shifted to 1625 cm^{-1} on solids P-n, and to 1626 cm^{-1} on solids G-n.

These higher wavenumbers prove that the chlorination of alumina enhances the strength of the Lewis sites [34], but the small shift does not allow a grading in order of acidic strength.

The density of Lewis sites (D_L μmol g^{-1}) over the samples evacuated at 420 K was deduced from the intensity of the 1455 cm^{-1} band, using an integral molar extinction coefficient ε of 2.2 cm μmol^{-1} [33]. All chlorinated solids have more Lewis sites than pure alumina. Samples G-n, which appeared devoid of Brönsted sites, have densities D_L higher than 200 μmol g^{-1}, except sample G-1b which was obtained from a highly dehydroxylated alumina and had only 150 μmoles Lewis sites per gram. Samples P-1 and P-2, which were also devoid of Brönsted sites, have D_L values similar to the G-n samples. However, lower D_L values, about 160 μmol g^{-1}, were found on samples P-3, P-4, P-5 and S-2. Accordingly, these solids were found to bear Brönsted sites (around 50 μmol g^{-1}). This suggests that hydrogen chloride converts some of the Lewis sites into Brönsted sites. The surface-HCl adduct appears only on those chlorinated solids which have been cooled with HCl in the gas phase and is rapidly destroyed when HCl is pumped off at ca 575 K or above.

Lewis sites on Al_2O_3-Cl were earlier pictured as $>$Al-O-AlCl$_2$ and were thought to combine with hydrogen chloride to give $>$Al-O-AlCl$_2$·HCl entities analogous to a Friedel-Crafts catalyst [10]. Recently, Webb [35, 36] gave a more realistic model of the Lewis site, involving four Cl anions and three coordinatively unsaturated Al cations. HCl may be adsorbed on such sites. Nevertheless the densities of sites measured here show that only a fraction of the Lewis sites may be transformed into the Brönsted form. However, our HCl-treated samples can catalyze the alkylation of isobutane with ethylene [17] meaning that their surface has very strong acidity, and the amount of retained HCl has a marked influence on the reaction, so that the Brönsted sites are presumably strong. But part of the chlorine is weakly retained, and the disappearance of the PyH^+ bands upon evacuation at 420 K most is likely due to volatility of pyridinium chloride at this temperature rather than weak acidity. With zeolites, for instance, grading of the hydroxyl groups by increasing acid strength is nicely obtained through gradual desorption of pyridine upon heating, but, in the case of chlorinated alumina, the strong Brönsted sites readily escape detection by this spectral method.

Lutidine adsorption

Because of steric hindrance at the nitrogen atom, the lutidine probe should react preferentially with the Brönsted sites, rather than with the Lewis sites of acidic catalysts. In fact, previous studies have detected a variety of species on such surfaces [37–39]. Physisorbed lutidine, with an absorption band at 1580 cm^{-1}, may be eliminated by pumping. Still, the spectra contain several bands overlapping in the region 1610–1650 cm^{-1}.

Thus, lutidine was adsorbed over some Al_2O_3-Cl samples and spectra recorded after pumping the excess base at 300 K are displayed in figure 6. The spectra in figure 7 were obtained after further evacuation at 420 K; the overall intensity decreased and maxima were slightly shifted.

The position of the main bands and their integrated intensities are presented in table IV. All spectra, including those of γ-alumina, feature a medium intensity band at 1577 cm^{-1} and a smaller one at 1605 cm^{-1} revealing a few lutidine molecules coordinated on Lewis sites [37]. Accordingly, the former band is noted L in table IV.

Spectra in the 1600–1650 cm^{-1} region were then decomposed into individual bands. As shown in figure 6, up to three absorptions could be distinguished, with maxima at about 1615–1620, 1625–1630 and 1641–1656 cm^{-1}. The band at 1641 cm^{-1}, which does not appear on γ-alumina, is intense only when the alumina sample has been treated with HCl (samples S and P)

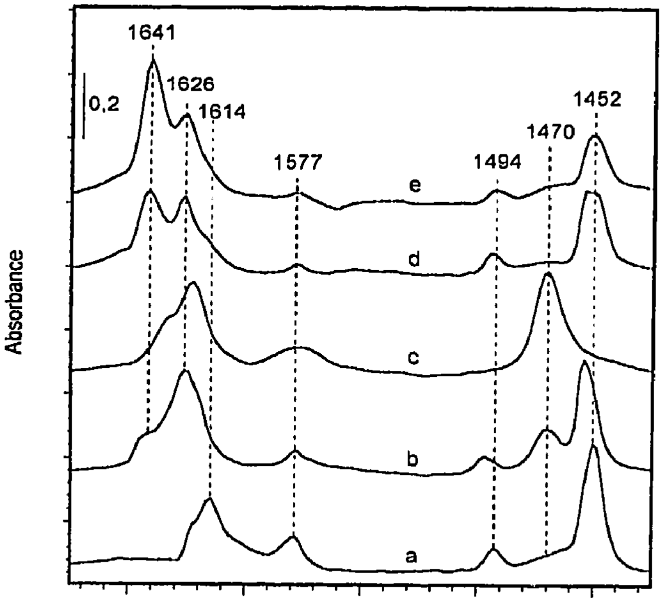


Fig 6. Infrared spectra of species remaining after lutidine adsorption onto chlorinated aluminas followed by evacuation at 300 K. **a)** γ-alumina; **b)** sample G-4; **c)** sample G-1; **d)** sample PH-1; **e)** sample S-1.

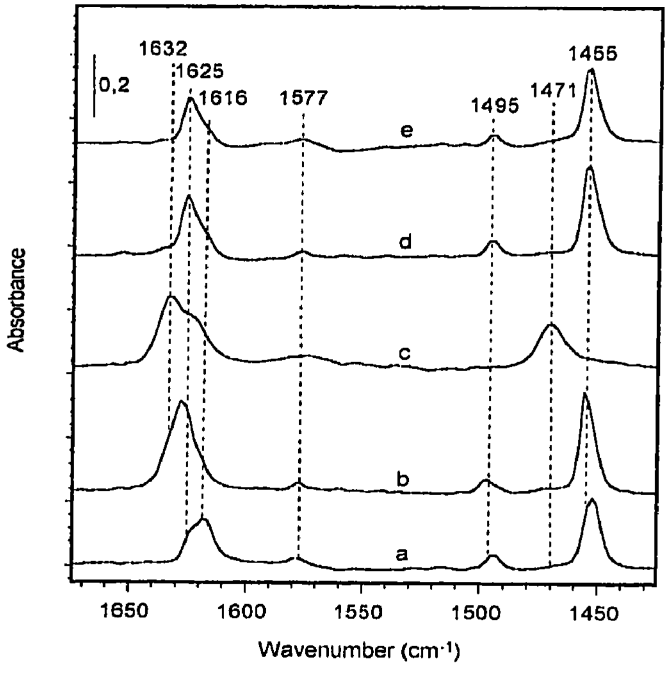


Fig 7. Infrared spectra of species remaining after lutidine adsorption onto chlorinated aluminas followed by evacuation at 420 K. **a)** γ-alumina; **b)** sample G-4; **c)** sample G-1; **d)** sample PH-1; **e)** sample S-1.

Table IV. Position of bands (cm^{-1}) and integral absorbance A ($cm^{-1}g^{-1}$) observed after lutidine adsorption and evacuation at 300 then 420 K.

Sample	*Chlorination reagent*[a]	T_{ev}[b]		*300 K*		*420 K*	
	T (K)	*(K)*		$\overline{v}$	*A*	$\overline{v}$	*A*
CK 300	None	670	*L*	1579	70	1578	20
			X_1	1614	170	1616	110
			X_2	1621		1622	
			B	–	–	–	–
G-4	$SOCl_2$/550	370	*L*	1577	50	1577	15
			X_1	–	– 330	–	– 240
			X_2	1625		1627	
			B	1643	60	–	–
G-1	CCl_4/550	570	*L*	1577	110	1575	50
			X_1	1622	305	1622	240
			X_2	1632		1633	
			B	1656	15	–	–
S-1	CCl_4/550 then HCl/550	370	*L*	1578	20	1577	20
			X_1	1616	240	1619	100
			X_2	1626		1625	
			B	1641 1657	405	–	–
PH-1	HCl + H_2/940	370	*L*	1577	10	1577	5
			X_1	1615	200	1619	120
			X_2	1626		1626	
			B	1641 1656	230	–	–

[a] See *Experimental section.*

and completely disappears upon pumping at 420 K. Following previous authors [36, 37] this band is ascribed to lutidinium ions formed on Brönsted sites, and therefore noted B in table IV. The same band may also appear at a higher wavenumber, but with a low and variable intensity, on samples treated according to the G-procedure (table IV). The occurrence of the B signal again shows that some HCl may be retained on those surfaces. As in the case for pyridine, the disappearance of the signal upon pumping at 420 K is ascribed to volatilization of the lutidinium chloride rather than to the weakness of the sites.

Most of the samples give rise to two additional bands at 1615–1625 cm^{-1}, which are much more resistant towards evacuation. They are tentatively considered as a compound signal noted X.

Over unchlorinated alumina, the low frequency component X_1 at 1614 cm^{-1} is more intense than the high frequency one X_2 at 1621 cm^{-1}. With solids S, P, G-1 and G-4, the X_2 component is more intense than X_1, so that the compound signal X looks rather similar on the chlorinated samples, except for a much higher intensity on solids G-4 treated with $SOCl_2$ and G-1 treated with CCl_4.

Attribution of the X signal (1618-1632 cm^{-1}) is not straightforward. In previous studies dealing with adsorption of lutidine on fluorinated alumina or H-zeolites, a band at 1640–1631 cm^{-1} has been attributed to the protonated base, while the band at 1618–1619 cm^{-1} has been assigned to lutidine adsorbed either onto Lewis sites [39] or weak Brönsted sites [38]. However, with the catalysts of this study, no pyridinium ions could remain adsorbed at 420 K, and the same should hold for lutidinium ions. In our opinion, all lutidine bands in the region 1618–1632 cm^{-1} should therefore belong to the same kind of species, probably coordinated lutidine.

The X_2 component which is found at 1621 cm^{-1} over γ-alumina shifts to about 1626 cm^{-1} upon chlorination, going as high as 1632 cm^{-1} for the CCl_4 treatment. The wavenumbers increase in the order:

$$\gamma\text{-}Al_2O_3 \ll \text{P-3} \approx \text{S-1} \approx \text{G-4} < \text{G-1}$$

Thus, like the ν_{8b} vibration of pyridine, but to a larger extent, signal X appears sensitive to the strength of the Lewis acid sites. For instance samples G-1 and G-4 look similar for the pyridine probe, but may be differentiated through their X signal. The spectra of lutidine in the 1450–1580 cm^{-1} region (fig 7) confirms the peculiarity of sample G-1.

Conclusion

IR spectra of pyridine and lutidine establish that chlorinated alumina bears Brönsted as well as Lewis acid sites. However, protonated species are detected only when the excess base has been removed at temperatures not exceeding 300 K. With lutidine, the intensity of the *B* absorption varies as follows:

$$\gamma\text{-Al}_2\text{O}_3 \ll \text{G-1a} < \text{G-4} < \text{P-3} < \text{S-1}$$

However no site density could be determined, ε being unknown. The fading of the signals upon heating at 420 K does not necessarily mean that the *B* sites are weakly acidic, but rather that HCl (pyridinium and lutidinium chloride as well) are loosely bound to the surface. More Brönsted sites are found when chlorination is performed with HCl (samples P and S) than with CCl_4 (G-1) or $SOCl_2$ (G-4). Also the various steps (eg, cooling and evacuation) following chlorination are important in this respect.

The solids investigated here were found to be efficient catalysts for the alkylation of isobutane with ethylene at 320 K [5] and the catalytic activity was ascribed to very strong acidity, presumably superacidity. Indeed, the unusually large shift in the *X* signal of lutidine adsorbed on the catalysts may be associated with a very high acidity. Catalysts prepared according to the G-procedure gave a 100% initial conversion of ethylene and differed only through their rate of deactivation, which varied as G-3 < G-2 < G-1 < G-4.

Catalyst S-1 was found to be similar to G-1, both in activity and stability [17]. It appears now that the catalysts also possess some Brönsted sites, with more Brönsted and less Lewis sites on solids S and P. Thus, alkylation with ethylene may be achieved by protonic as well as Lewis sites.

However, the alkylate obtained with catalyst S-1 contained distinctly more C_6 and less C_5, C_8 etc, than with the other catalysts. Selectivity for monoalkylation versus other processes (successive alkylation, oligomerization or cracking) depends on a high rate of desorption of the dimethylbutyl cation through hydride transfer from isobutane. In the series considered, the selectivity for monoalkylation ranked as:

$$\text{G-3} < \text{G-2} < \text{G-4} < \text{G-1} < \text{S-1}$$

This is roughly in agreement with the number of Brönsted sites measured by spectroscopy. Therefore the ability of the catalyst to provoke H-transfer seems connected with the density of Brönsted sites.

Hence, our results are in line with earlier studies, particularly with those dealing with alkylation of isobutane and isomerization of normal alkanes with an $AlCl_3$ slurry catalyst [40]. Careful studies showed the unavoidable occurrence of small quantities of HCl in this so-named Friedel-Crafts catalyst. A recent patent claims that the lifetime of an alkylation catalyst made of $AlCl_3$ deposited on alumina is increased when a chlorinated compound (eg, butyl chloride) is added to the feed [41]. The organic chloride ensures continuous regeneration through release of HCl. Primet evidenced the benefit of HCl in the feed while isomerizing *n*-butane at low-temperature over chlorinated alumina [16]. In industrial practice, long-life Pt-Al_2O_3-Cl hydroisomerization catalysts are sustained by continuous in situ production of HCl from halogenated organic compounds. Similarly, Myers [15] established that the efficiency of high temperature HCl-chlorinated alumina for *n*-C_4 isomerization and hydrocracking was highly dependent on carefully controlled cooling in the presence of HCl. All these observations are in line with our finding that Al_2O_3-Cl retaining HCl are more efficient and selective in alkylation of isobutane with ethylene and the only effective catalyst in alkylation of butene.

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