Chlorinated Alumina

Acidic Properties and Catalytic Activity towards n-Butane Isomerization

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 γ -Al₂O₃ has been chlorinated by CCl₄ at 573 K in order to increase its acidity. Different physical methods, including infrared spectroscopy, thermogravimetry and thermodesorption of pyridine, have been used to calculate the actual number of acidic sites, according to their strength. Comparison with samples treated with HCl or AlCl₃ leads to the conclusion that stronger Lewis sites are in the form of grafted AlCl₃. n-Butane isomerization has been performed on such solids. Reaction occurs without the presence of metal and the higher the acidity the higher the activity and selectivity.

Alumina is one of the most widely used supports in heterogeneous catalysis. Its preparation and properties have been studied extensively.^{1, 2} By calcination at high temperatures, most of the OH groups are removed, leading to incompletely coordinated aluminium ions that behave like Lewis acidic centres. Despite the fact that some OH groups are still present on the surface, they are not acidic in nature. Adsorption of basic molecules like pyridine has clearly demonstrated that no Brønsted acidity has been evidenced, whereas Lewis centres have always been observed. Alumina may be modified by incorporation of Cl^- [ref. (3)] or F^- [ref. (4)] ions that increase the acid strength, but not the total number of sites.

Alkane isomerization may occur *via* acid-catalysed reactions, in particular with solid-state Lewis acids such as alumina halides or boron fluoride.⁵ On oxide catalysts such a reaction takes place provided the acidity is strong enough. Usually a bifunctional catalyst is preferred, that possesses both acidic and metallic properties, yet on metal-free supports the reaction can effectively proceed, suggesting a carbonium-ion mechanism.⁶

During cracking operations in petroleum processes many light molecules like propane and butane are formed.⁷ Butane is not a top primary chemical. Isobutane, on the contrary, can be used as a feedstock for alkylation of aromatics or ethylenics. Isomerization of n-butane proceeds *via* the formation of a primary carbonium ion and the low stability of this carbonium ion is responsible for the slow butane isomerisation.^{7, 8}

The aim of this work is related to n-butane isomerization on γ -alumina that has been modified by chlorine incorporation from various compounds, *i.e.* CCl₄, AlCl₃ or HCl, to compare it with AlCl₃ grafted alumina and to determine the acidity. The ultimate goal is to relate isomerization to surface acidity.

Experimental

Catalyst Modification

GFS 400 γ -alumina from Rhône Poulenc and Degussa Aerosil silica were used. One home-made alumina was obtained by calcination at 773 K of boehmite from Bayer. This

n-Butane Isomerization over Chlorinated Alumina

catalyst	surface area/m² g ⁻¹	particle size/µm	pore diameter/Å	X-ray structure	impurities (ppm)
alumina GFS 400 (Rhône Poulenc)	200		130	γ	Na ₂ O:100 MgO:50 CaO:50 S:280
home-made alumina from Boehmite calcination	130	0.1–2	25	γ	Na ₂ O:2000
silica Aerosil 200 (Degussa)	200	0.12	non-porous		S:50

 Table 1. Characteristics of catalysts

contains 1500 ppm of sodium (table 1). Al_2O_3 (or silica) samples were first pretreated in flowing dry oxygen up to 773 K and then evacuated overnight at the same temperature. Solids were then contacted with chlorinated compound vapours.

HCl

Chlorination with HCl was performed at 473 or 573 K with dry gas ($P_{\rm HCl} = 10$ Torr) followed by evacuation at 373 or 473 K (1 Torr ≈ 133.3 Pa).

AlCl₃

Interaction of activated alumina with $AlCl_3$ was performed *in situ* at temperatures between 298 and 393 K. In this temperature range aluminium chloride has a low vapour pressure, but it was sufficient for reaction with alumina to occur. After grafting $AlCl_3$ on Al_2O_3 or SiO_2 , the samples were evacuated at 573 K in order to remove excess unreacted $AlCl_3$ and HCl formed during surface reaction.

CCl_4

Silica could not be chlorinated by CCl_4 . On the other hand, alumina was contacted with CCl_4 at 573 or 473 K. The temperatures were chosen in accordance with the previous work of Mathieu and coworkers.⁹ These authors demonstrated that at 473 K there is a surface reaction leading to OH substitution by Cl atoms and removal of surface oxygen atoms with the formation of strong Lewis centres. At 573 K there is more severe reaction involving a bulk attack of solid with the formation of AlCl₃. If chlorination time exceeded 30 min at 573 K, loss of aluminium in the form of AlCl₃ was observed.

In both cases evacuation at 473 K for a few hours followed CCl₄ treatment.

Experimental Methods

Spectroscopy

I.r. spectra were recorded at room temperature with a Perkin-Elmer 580A spectrophotometer. Samples of *ca.* 20–50 mg were compressed into self-supporting wafers of 18 mm diameter (pressure 40 MPa). All the above procedures (modification of supports) were performed *in situ* in the i.r. cell and used carefully dried HCl or CCl_4 . Pyridine adsorption was performed at room temperature.

A. Melchor et al.

reaction temperature: 473–773 K nC_4 pressure: 0.14–0.18 atm^a H_2 pressure: 0.86–0.82 atm^a catalyst weight: 0.1–1 g time contact: 0.4–1 s column: 20% propylene carbonate on chromosorb PAW 60/80 oven temperature: 293 K vector gas: N₂ (1 cm³ min⁻¹)

 $a \ 1 \ atm = 101 \ 325 \ Pa.$

Kinetics

Gas chromatography was used to analyse products and reactants with a differential reactor at atmospheric pressure. The catalyst was laid in a very thin bed in a U-shape quartz or Pyrex microreactor, and continuously flushed with an nC_4 -H₂ mixture using a H₂/C₄ ratio of *ca*. 7 (see table 2).

Gravimetry

Some additional gravimetric experiments were performed with a Sartorius thermobalance allowing *in situ* pretreatment (catalyst weight = 70 mg, sensitivity = 1 μ g).

Results

Quantitative Acidity Determination

Pyridine is the most widely used base for checking acidity: its i.r. spectrum shows numerous sharp bands; some of them are characteristic of pyridinium (Brønsted sites) whereas others reveal electron-deficient (Lewis) sites.¹⁰ As yet there is very little literature about the actual number of acidic sites with respect to their strength. In order to compare different aluminas (chlorinated with various compounds) and to relate acidity to activity we performed first a calibration of adsorbed pyridine in three steps: (i) an i.r. study of pyridine stability, (ii) an i.r. study of optical density of pyridine *vs*. adsorbed quantities (adsorption of known amounts) and (iii) gravimetric measurements.

Pyridine Adsorption

After O_2 and vacuum treatment at 773 K of the GFS 400 γ -alumina, pyridine was adsorbed at room temperature (saturated vapour pressure). The i.r. spectrum showed strong perturbations of OH groups, but no pyridinium ions were observed. The gas phase was then removed and desorption was performed during 1 h at temperatures from 423 to 923 K. Fig. 1(*a*) shows the evolution of the intensity of the 19*b* mode (1455 cm⁻¹, pyridine adsorbed on Lewis sites) as a function of the temperature of desorption of pyridine. The absorbance of the 1455 cm⁻¹ band was expressed per gram of catalyst taking into account the weight of the pellet. It can be seen that even after desorption of pyridine at 923 K minute amounts of base are still adsorbed on Lewis sites.

Pyridine Desorption

In gravimetric experiments performed in a different way, pyridine was admitted at room temperature onto the same Al_2O_3 sample activated at 773 K. Pyridine was removed by heating under vacuum at increasing temperature. The same procedure in the i.r. cell was



Fig. 1. Thermal stability of pyridine adsorbed on alumina (●, GFS 400; ○, Na containing solid).
Evolution of the absorbance of the 19b mode (pyridine on Lewis centres) vs. the temperature of pyridine desorption. There was no irreversible pyridine adsorption at 323 K on silica.

also used to follow pyridine adsorption by i.r. spectroscopy. Fig. 2 gives the amount of pyridine adsorbed per gram of catalyst as a function of the absorbance of the 1455 cm⁻¹ band for the same temperatures of desorption of pyridine: a linear relationship is observed. In a third experiment, known small amounts of pyridine were adsorbed at room temperature on an Al₂O₃ sample previously treated under oxygen and vacuum at 773 K. After adsorption of each dose an i.r. spectrum was recorded. The absorbance of the 1455 cm⁻¹ band was measured and expressed per gram of catalyst. A linear relationship between the absorbance of the 19b band and the amount of adsorbed pyridine was also observed. It can be concluded that Beer's law is satisfied in the concentration range studied. From the slopes of the two straight lines obtained it can be deduced that an absorbance equal to unity corresponds to 1019 molecules of pyridine adsorbed per gram of catalyst. Taking into account the specific area of the sample, measurement of the absorbance of the 1455 cm⁻¹ band gives access to the number of acid sites per surface unit able to chemisorb pyridine at a given temperature. The total number of Lewis sites was deduced from the intensity of the 1455 cm⁻¹ band after desorption of pyridine at 423 K. Pyridine remaining on the sample after a vacuum treatment at 623 K is assumed to be coordinated to strong Lewis acid sites; the number of these sites was determined from the intensity of the 19b mode after evacuation at 623 K (table 3).

Acidic Properties and Isomerization Activities

According to the procedure used for alumina, the number and strength of Lewis acidic centres were determined as well as the catalytic activity in n-butane isomerization. Results are summarized in table 3 (note that the reaction was performed either at 659 or 563 K, depending upon the activity of the catalyst).

1897



Fig. 2. Pyridine adsorption on γ -Al₂O₃ GFS 400. Relationship between gravimetric and i.r. measurements, for the same temperatures of pyridine desorption.

absorbance (arbitrary units g⁻¹ catalyst)

10

5

50

0

solid	total sites (no. per nm ²)	strong sites (no. per nm²)	isomerization activity /mol h ⁻¹ g ⁻¹	isobutane selectivity (%)	T/K
(1) $Al_{2}O_{3}$	0.6	0.27	0.23×10^{-4}	40	659
(2) $Al_2O_3 + Na^a$	0.21	0.04	$0.08 imes 10^{-6}$	1	659
(3) $Al_2O_3 + HCl$	0.76	0.48	$0.30 imes 10^{-4}$	30	659
(4) $Al_2O_3 + CCl_4$	1.5	0.6	0.38×10^{-4}	80–90	563
(5) $Al_2O_3 + AlCl_3$	1.23	1.04	0.91×10^{-4}	90–97	563
(6) $SiO_2 + AlCl_3$	0.75	0.38	$0.30 imes 10^{-4}$	80	563

Table 3. Density of Lewis centres and rate of n-butane isomerization for the solids studied (extrapolated to zero time)

^a Home-made alumina containing 1700 ppm of soda. Other products were methane, ethane, propane and but-2-enes.

GFS 400 y-Al₂O₃

The solid was inactive below 573 K in our experimental conditions. Butane isomerization took place at 659 K with a selectivity of ca. 40% when the activity was stabilized. The other products were butenes (50%) and some cracking products (ca. 10%)).

Soda-containing Alumina

The solid showed an extremely low catalytic activity even at 659 K, moreover, the isomerization selectivity was only 1%. The reactivity resulted essentially in butenes, whose concentrations corresponded almost to thermodynamical equilibrium. Some cracking occurred, but this decreased gradually and became almost null after 8-10 h.

n-Butane Isomerization over Chlorinated Alumina

GFS 400 Al₂O₃ chlorinated by HCl

The starting Al_2O_3 , activated at 773 K under O_2 was heated in HCl at 573 K. The i.r. spectrum revealed pyridinium ions (1535 cm⁻¹), that were promptly eliminated by evacuation at 423 K. After desorption at higher temperatures the absorbance of the pyridine band at 1455 cm⁻¹ (19*b* mode) allowed the determination of the number of Lewis acidic centres: the proportion of stronger sites increased by 80%. Nevertheless the isomerization was still very low and was comparable to that of alumina. It should be noted that many butenes also appeared, as in the preceding case. In conclusion, chlorination by HCl was not efficient, despite the modification of surface acidity. There seems to be a second factor including 'quality of sites': strength is not sufficient to account for activity.

Chlorination of GFS 400 Al₂O₃ by CCl₄

After desorption at 773 K, the GFS 400 alumina was contacted with CCl₄ vapour at 573 K for 30 min, then desorbed at 473 K. The solid obtained was completely dehydroxylated since no ν (OH) bands were observed in the i.r. spectrum. Pyridine was adsorbed at 298 K and the sample was evacuated at 423 K. The number of acidic centres, according to the intensity of the 1455 cm⁻¹ band, was found to be 1.5 nm⁻², whereas the number of stronger ones increased by a factor of two (table 3). At the same time the solid was very active and a temperature of 563 K was sufficient to measure its activity. Despite this, the catalyst deactivated rapidly, especially within the first 2 h [fig. 3(*a*)], then the deactivation became linear. Catalytic activity was measured by extrapolating the linear part of the deactivation curve to zero time. Selectivity of the CCl₄-treated material was higher than 80%, the other products being dehydrogenated and cracked compounds.

GFS 400 Al₂O₃ treated by AlCl₃

Previous work performed in our laboratory has shown that chlorination of alumina by CCl_4 at 573 K leads to a loss of weight and formation of $AlCl_3$, which sublimes.⁹ Thus, in order to test whether nascent $AlCl_3$ is able to chemisorb, the interaction of alumina with $AlCl_3$ was also studied.

GFS 400 Al_2O_3 evacuated at 773 K was contacted with $AlCl_3$ vapour in excess at 393 K then desorbed at 573 K in order to compare results with those obtained by CCl_4 treatment. Adsorption of pyridine followed by desorption at 423 K showed in the i.r. spectrum the presence of some pyridinium ions that were eliminated at 423 K *in vacuo*. The pyridine coordinated to Lewis centres was observed and the position of the i.r. bands revealed that the sites were very strong. After calculation, it was observed that both the total number and population of stronger sites increased markedly (table 3).

The catalyst obtained was very selective in isomerization (90–97%). Initial deactivation was not observed because the catalyst lost its activity very slowly and linearly [fig. 3(b)].

Silica treated with AlCl₃

In the preceding sample, AlCl₃ reacted with the alumina surface, *i.e.* with OH groups, leading to AlCl₃ being grafted onto the surface. That process can occur on other supports containing OH groups. Silica possesses hydroxy groups that are relatively inert towards chemicals, but some AlCl₃ reacts with the OH groups, as revealed by i.r. spectroscopy. The absorbance of the v(OH) band at 3740 cm⁻¹ was gradually removed by contacting SiO₂ with AlCl₃ at 393 K. After desorption at 573 K pyridine was adsorbed onto such a solid. No Brønsted sites were observed, whereas many pyridine molecules coordinated to Lewis centres were detected. Even after desorption at 773 K some molecules were still

A. Melchor et al.



Fig. 3. Isomerization of n-butane at 563 K on chlorinated alumina: ●, γ-Al₂O₃ GFS 400 treated with CCl₄ at 573 K for 30 min; ○, γ-Al₂O₃ GFS 400 treated with AlCl₃ in excess.

present, proving that these centres were very strong (note that pyridine is completely desorbed at 373 K on silica, which does not show any Lewis centres).

On such a solid, the reaction was operated at 563 K and, as expected, the catalyst was highly active and very selective in isomerization (table 3), the performances of these samples were comparable to those of the CCl_4 -treated alumina. In the absence of treatment by $AlCl_3$, silica is inactive in butane isomerization, even at 659 K. At that temperature the activity of untreated silica was very low and gave essentially butenes with a selectivity of 97%. The isomerization rate was calculated to be ca. 0.05×10^{-6} mol h⁻¹ g⁻¹, *i.e.* very close to that of the sodium-containing alumina.

Discussion

The results obtained clearly show that isomerization activity is closely related to Lewis activity and that there is a minimum required acidity.

 Al_2O_3 alone is not active at 563 K and a higher temperature had to be used in order to achieve some activity. The sodium-containing alumina was completely inactive in isomerization (selectivity of *ca.* 1%), whatever the temperature: the major products were butenes (53%), the concentration of which corresponds to thermodynamic equilibrium. The balance was composed of methane, ethane and propane. On the other hand, γ -Al₂O₃ that contacted HCl revealed a great increase of stronger sites, but activity was not substantially enhanced. Thus the strength of the centres alone is not sufficient to explain activity: there is another parameter that has to be accounted for as Al₂O₃ that had been chlorinated by CCl₄ proved to be very active, although the number of sites was comparable to that obtained with HCl treated Al₂O₃. It must be noted that chlorination by CCl₄ is completely different from the reaction of HCl with Al₂O₃.

If reaction of alumina with CCl_4 is performed at 573 K, attack of the lattice occurs, leading to the formation of nascent $AlCl_3$. At that temperature, it sublimes and the underlying Al atoms can also come into contact with Cl atoms. The solid chlorinated by CCl_4 at 573 K is very active. Therefore, isomerization activity must be connected to the presence of $AlCl_3$: its presence leads to a special kind of site having a strong electron deficiency on the aluminium atom. In that sense one should be able to obtain a similar catalyst by contacting alumina (or silica) with $AlCl_3$ directly. The results in table 3 agree with that hypothesis and with works previously published.¹¹⁻¹² Thus CCl_4 reacts with

1899



Fig. 4. Correlation between the rate ('n-butane isomerization and the number of strong Lewis acid sites per surface unit: (a) less ac ve catalysts (reaction at 659 K); (b) more active catalysts reaction at 563 K).

surface oxygen atoms and leads to $AlCl_3$, which is then grafted on the remaining OH groups and forms



species. Concerning butane isomerization, Pines *et al.* noted, that 'evidence points to a hydroxy aluminium halide as the active catalyst'⁵ and that aluminium oxy-halide is a very strong acidic centre. If $AlCl_3$ is contacted with silica there is also creation of

$$\geq$$
Si-O-Al \leq_{Cl}^{Cl}

species at the expense of silanol groups.¹³ In both cases the strength of sites must be comparable, as well as their activity and selectivity, as reported in table 3. On the other hand, grafting of $AlCl_3$ onto alumina leads to the most active solid, for most of the OH groups are substituted by $-AlCl_2$ species. Thus the number of stronger sites increases. A careful examination of table 3 shows that activity increases with stronger site population. Fig. 4(*a*) and (*b*) show that behaviour.

Conclusion

Alumina is a solid-state acid. It contains Lewis-acidic centres having a wide range of strength as revealed by i.r. investigations of pyridine absorption. The presence of strong sites is needed in order to obtain catalysts efficient for alkane isomerization. When the solid does not possess such sites it is completely inactive in isomerization. This is the case for Na-contaminated alumina, where the Lewis sites are blocked by the alkaline cation, and for silica there are no Lewis sites at all. The major products are butenes, the concentration of which corresponds closely to thermodynamical ratios. On the contrary, when solids are acidified by chlorine incorporation there is a strong Lewis acidity enhancement and appearance of isomerization activity. Both phenomena are surely correlated.

On the other hand, the origin of chlorine is not similar. Alumina contacted with HCl gives strong modifications in acidity despite small changes in activity. With $AlCl_3$ (pure or produced by CCl_4), the most active catalysts are obtained either for alumina

or for silica and they are also the more acidic. In fact, active catalysts in isomerization are solids containing

$$O-Al \leq Cl Cl$$

grafted onto the surface. Such a species consists of an accessible aluminium atom whose electron deficiency has been greatly enhanced. Such a hypothesis has already been suggested by Franck *et al.*¹⁴ concerning isomerization of light paraffins. The authors had anchored ethyl aluminium sesquichloride onto alumina (EASC) that liberated HCl. Further reaction of HCl onto

 $Al-O-Al < Cl leads to Al-O-AlCl_3 + H^+.$

They showed that the Lewis site is an inactive one, whereas the active site is a superacid. They were led to that conclusion by observing an induction period during alkane isomerization.

In our case, the isomerization proceeded as soon as the reactants were admitted. Thus the absence of an induction period may suggest that the nature of the active sites is different in the two catalytic systems. Nevertheless a dechlorination of the support has been observed during isomerization. As a consequence, HCl might react with

$$Al-O-AlCl_2$$

species, leading to a superacid site identical to that postulated by Franck et al.¹⁴

For active isomerization catalysts, strong Lewis-acid sites have been evidenced. They can abstract hydride ions from the hydrocarbons. They can also be converted into Brønsted centres by addition of HCl; the very labile proton is able to attack the butane molecule giving a species containing so-called pentavalent carbon.¹⁵

Additional experiments concerning the influence of the introduction of HCl in the course of the reaction are necessary for determining the nature of the sites responsible for the activity during the reaction.

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