Solid Superacids: The Alumina/ZrCl_a System

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The physico-chemical and catalytic properties of alumina exposed to $ZrCl_4$ vapour have been studied. It was found that $ZrCl_4$ reacts with both basic surface OH groups and exposed O^{2-} ions forming Lewis superacid centres as well as Brønsted acid sites. The mechanism of *n*-pentane low-temperature isomerization involving H⁻ abstraction from the alkane has been postulated.

Acidic systems of an acid strength greater than that of pure sulfuric acid ($H_0 = -11.93$) are defined as superacids.¹ Owing to their high acid strength they are able to protonate very weak bases, such as saturated hydrocarbons, causing their transformation even at room temperature. The best known superacids are the following solutions: HSO_3F-SbF_5 ,² $HF-SbF_5$ ³ and $HF-TaF_5$.⁴ According to Olah *et al.*⁵ a reactive proton originating from a superacid attaches to the single C—H bond of an alkane to form the pentacoordinated carbonium ion:

$$\mathbf{R} - \mathbf{C}\mathbf{H}_3 + \mathbf{H}^+ \longrightarrow \begin{bmatrix} \mathbf{R} - \mathbf{C}\mathbf{H}_2 - \mathbf{H} \end{bmatrix}^+ \xrightarrow{\mathbf{R}} \mathbf{R} - \mathbf{C}\mathbf{H}_2^+ + \mathbf{H}_2$$

Such an unclassical cation is unstable and decomposes immediately with the formation of hydrogen and a carbenium ion. The latter undergoes further transformations leading to isomerization, alkylation or cracking reaction products.

Superacids also include a variety of solid systems such as metal oxides treated with SbF_{5} ,⁶ AlCl₃-treated alumina or macroporous sulfonic resin (Amberlyst),^{7,8} the perfluorinated resin Nafion-H of Du Pont,⁹ physical mixtures of aluminium halides with metal halides or sulfates,¹⁰ as well as sulfuric acid-treated hydroxides (or oxides) of iron, titanium and zirconium.¹¹⁻¹³ Recently, a new superacid system based on silica treated with sulfuryl chloride has been reported.¹⁴

All these solid superacids are able to initiate the *n*-alkane transformation at low temperatures. The mechanism of the reaction initiation depends on the nature of a given system. Nafion-H⁹ or aluminium trichloride-treated Amberlyst,⁷ being Brønsted acids, behave like solutions of typical superacids, for example, HSO_3F-SbF_5 . The mode of action of other systems that are considered Lewis-type superacids is still controversial.

In this case, initiation of an alkane reaction is frequently postulated to involve H^- abstraction from the reacting molecule by the Lewis superacid centre.^{15,16} However, some even argue against the possible existence of Lewis superacid sites.¹⁷ It is claimed that such centres are so reactive that even a trace of water converts them into secondary Brønsted sites which are responsible for the catalytic activity of the system.

In our previous work we have proposed a mechanism for superacid centre formation on the surface of alumina treated with $AlCl_3$ vapour. We found that the superacid sites are of Lewis nature and they are able to withdraw the hydride anion from *n*-alkanes.^{8,18} This study is a continuation of research on superacid formation by the reaction of Lewis acid vapour with alumina, and deals with the $Al_2O_3/ZrCl_4$ system.

Experimental

Aluminium oxide was prepared by calcination of aluminium hydroxide at 823 K in an air stream. Aluminium hydroxide was synthesized by hydrolysis of aluminium isopropoxide (POCh Gliwice). Silica-aluminas with alumina contents of 87 and 30 wt.% were obtained by calcination at 823 K of coprecipitated aluminium and silicon hydroxides obtained from isopropyl alcohol solutions of aluminium isopropoxide and silicon ethoxide (Fluka), respectively. The silica used in some experiments was supplied by Degussa.

Superacid synthesis was performed in the following manner: A known quantity of alumina (1 g) was calcined for 1 h at 773 K under reduced pressure $(10^{-2} \text{ Torr}^{\dagger})$. Then the sample was cooled and contacted with water vapour of a partial pressure equal to the saturated vapour pressure at 298 K. After 10 min the water vapour was evacuated and the sample was heated to a desired temperature and calcined for 2 h in vacuo. On cooling the sample to room temperature, ZrCl₄ was introduced in the stream of dry, oxygen-free nitrogen below the alumina bed. Then the system was evacuated and heated to 673 K. In such conditions, ZrCl₄ was sublimed through the alumina bed. To avoid physical adsorption of $ZrCl_4$, the heating and evacuation were continued for 1 h. Then the catalyst was transferred either to the reactor or to the vessels for adsorption experiments. The catalysts with supports other than alumina (silica-aluminas, silica) were prepared according to the above procedure. The chemical compositions (i.e. Cl and Zr content) of the catalysts obtained were examined. For Cl analysis, the catalysts were boiled with concentrated HNO₃ and the resultant solution was then analysed by Volhard titration. The quantity of Zr in the solution was measured by UV spectroscopy.

Acidic Properties

Ammonia, pyridine and 2-ethylpyridine adsorption followed by IR spectroscopy were used to study the acidic properties of the catalysts.

The catalyst carrier was pressed into a thin wafer of 18 mm in diameter (0.02 g) and placed in an IR cell. After evacuation (10^{-4} Torr) the wafer was calcined in the same way as during the catalyst synthesis. When the calcination procedure was completed, the cell was cooled down to room temperature and the IR spectrum was recorded. Next the cell was filled with pure (oxygen- and water-free) nitrogen and ZrCl₄ was placed in a movable vessel. After evacuation, both wafer and vessel with ZrCl₄ were transferred for 15 min to the heating zone of the cell. At 673 K, ZrCl₄ sublimed and its vapour

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^{† 1} Torr = (101 325/760) Pa.

reacted with the wafer. On cooling the cell (to 298 K), the IR spectrum was taken. Then the ammonia vapour (100 Torr), pyridine or 2-ethylpyridine (partial pressure equal to the saturated vapour pressure at 298 K) were introduced into the cell. After 15 min of adsorption the system was evacuated and the IR spectrum was recorded. Then the sample was heated *in vacuo* to 373, 423, 523 and 573 K and the respective IR spectra were registered. For all the measurements, a spectro-phometer Specord 75 IR (Carl Zeiss, Jena) was used.

The indicator adsorption method for the acid strength estimation could not be employed since all the catalysts studied turn dark in the presence of the Hammett indicator solvent (benzene).

One-electron Acceptor and One-electron Donor Properties

The ability of a catalyst under study to donate or to accept an electron was examined by using electron paramagnetic resonance (EPR) spectroscopy to follow the adsorption of perylene and tetracyanoethene.^{19,20} In the presence of oneelectron acceptor (donor) centres, perylene (tetracyanoethene) molecules are transformed into cation radicals (anion radicals). The quantity of ion radicals formed was measured by means of an EPR X-band spectrometer (Jeol 3X). For EPR measurements, catalysts were contacted in an atmosphere of oxygen- and water-free nitrogen with saturated benzene solutions of perylene and tetracyanoethene. In some experiments before perylene introduction onto the catalyst, surface oxygen was pre-adsorbed (298 K, 200 Torr).

Catalytic Properties

Transformations of pentane and butane were studied. After synthesis, the catalyst (1 g) was transferred *in vacuo* into a batch reactor (volume 61 cm³) which was an integral part of the catalyst-synthesis unit. Then the reactor was heated to the desired temperature and the reactants were admitted (pressure of *n*-pentane 24.4 kPa, pressure of *n*-butane 53 kPa). The initial reaction rate (*i.e.* the rate extrapolated to zero contact time) was taken as a measure of the catalytic activity. Reaction products were analysed by means of gas chromatography using a squalane capillary column (30 m).

Results

The catalyst obtained as a result of $ZrCl_4$ vapour reaction with alumina is able to catalyse *n*-pentane and *n*-butane transformation even at room temperature. Isobutane was found to be the sole product of the *n*-butane reaction while isopentane, isobutane and isohexanes were formed from *n*pentane. Typical results of *n*-pentane transformations are presented in Fig. 1.

The results of catalytic activity measurements are presented in Table 1.



Fig. 1 Pentane conversion into isobutane (\bigcirc) , isopentane (\triangle) and isohexanes (\square) vs. reaction time. Batch reactor, reaction temperature 298 K, pentane pressure 24.4 kPa, catalyst: 1 g of Al₂O₃ (calcination temperature 773 K)/ZrCl₄

The catalysts obtained by $ZrCl_4$ vapour reaction with silicaaluminas fail to catalyse the *n*-butane isomerization. However, they were able to initiate the *n*-pentane reaction. The SiO₂/ZrCl₄ catalytic system was found to be inactive.

IR Measurements

Introduction of $ZrCl_4$ onto the surfaces of the carriers results in the disappearance of IR bands characteristic of the surface OH group vibrations (see Fig. 2): 3730 and 3670 cm⁻¹ for alumina,²¹ 3730 and 3600 cm⁻¹ for silica–aluminas,²² 3740 and 3700–3500 cm⁻¹ for silica.²³

The results of ammonia adsorption are partly presented in Fig. 3 (in the $1800-1200 \text{ cm}^{-1}$ range).

Al_2O_3

Ammonia adsorption [Fig. 3(*a*) and (*d*)] results in the appearance of new bands in the IR spectrum: 3560, 3390, 3350, 3250, 1610, 1470 and 1220 cm⁻¹. After evacuation at 523 K complete desorption of NH₃ takes place.

Al₂O₃/ZrCl₄

On adsorption of ammonia at 298 K, the following bands appear in the IR spectrum [Fig. 3(g)]: 3320, 3150, 3050, 1610, 1410 (with shoulder at 1435) and 1230 cm⁻¹. Heating to 373 K results in 3270 cm⁻¹ band separation, an intensity decrease of the bands at 3320 and 1410 cm⁻¹, disappearance of the bands at 3150 and 3050 cm⁻¹. As a consequence of temperature elevation to 423 K, the band at 1410 cm⁻¹ disappears. After desorption at 573 K the bands at 3330, 3260 and 1600 cm⁻¹ can be still observed.

$30 \text{ wt.\% Al}_2O_3-70 \text{ wt.\% SiO}_2$

Upon adsorption of ammonia at 298 K the following bands can be seen in the IR spectrum [Fig. 3(b) and (e)]: 3730 and

Table 1 Results of alkane isomerization (batch reactor, 1 g of catalyst, 24.4 kPa *n*-pentane, 53 kPa *n*-butane, ZrCl₄ evaporation at 673 K)

	temperature/K		initial reaction rate/min ⁻¹	
catalyst	reaction	calcination	pentane	butane
$Al_2O_3/ZrCl_4$	298	773	0.166	0.020
	333	773	0.166	
	333	673	0.095	_
	333	873	0.130	
	333	973	0.100	
87 wt.% Al ₂ O ₃ -13 wt.% SiO ₂ /ZrCl ₄	298	773	0.110	0.000
30 wt.% $Al_{2}O_{3} - 70$ wt.% $SiO_{2}/ZrCl_{4}$	298	773	0.040	0.000
SiO ₂ /ZrCl ₄	298	773	0.000	0.000



Fig. 2 Infrared absorption spectra of (a) $Al_2O_3/ZrCl_4$, (b) Al_2O_3 , (c) 30 wt.% Al_2O_3 -70 wt.% $SiO_2/ZrCl_4$, (d) 30 wt.% Al_2O_3 -70 wt.% SiO_2 , (e) $SiO_2/ZrCl_4$, and (f) SiO_2

3600 cm⁻¹ (both originated from the OH group), 3250, 1620 (originated from Si-O bond²⁴) and 1440 cm⁻¹. Heating to 573 K results in the disappearance of all IR bands originated from the adsorbed ammonia.

30 wt.% Al₂O₃-70 wt.% SiO₂/ZrCl₄

On adsorption of ammonia at 298 K the following bands appear in the IR spectrum [Fig. 3(h)]: 3330, 3250, 3150, 3050, 1605, 1550 (low intensity) and 1410 cm^{-1} . Heating the sample to 473 K results in the disappearance of the 1410 cm⁻¹ IR band. After desorption at 523 K all ammonia is removed from the surface.

SiO₂

On ammonia adsorption at 298 K [Fig. 3(c) and (f)] a new band appears with a maximum at 3550 cm⁻¹. Desorption at 573 K removes all of the ammonia adsorbed on the silica surface.

$SiO_2/ZrCl_4$

Adsorption of ammonia at 298 K results in the appearance of new IR absorption bands [Fig. 3(i)] at 3445, 3340, 3250, 3150, 3050, 1600, 1550 and 1410 cm⁻¹. Upon heating to 423 K the bands at 3150, 3050, 1600 and 1410 cm^{-1} disappear while the weak bands at 3445, 3350, 3260, 1550 and 1537 cm⁻¹ remain in the spectrum.

The results of pyridine adsorption (in the 1800-1200 cm⁻¹ range) are presented in Fig. 4.

Al₂O₃

Pyridine adsorption at 298 K results in the appearance of the following new IR bands [Fig. 4(a), (c) and (d)]: 3700, 3550, 3080, 3060, 1610, 1590, 1570, 1490 and 1445 cm⁻¹. Desorption at 473 K reduced considerably the intensity of these bands.

Al₂O₃/ZrCl₄

On adsorption of pyridine the following bands appear in the IR spectrum [Fig. 4(b), (e) and (f)]: 3080, 3060, 1610, 1575, 1490, 1445 and 1220 cm⁻¹. As a consequence of temperature



Fig. 3 Infrared adsorption spectra of (a) Al₂O₃, (b) 30 wt.% Al_2O_3-70 wt.% SiO₂, (c) SiO₂, (d)-(f) ammonia adsorbed and evacuated at 298 K on supports (a)-(c), respectively, and (g)-(i) ammonia adsorbed and evacuated at 298 K on Al₂O₃/ZrCl₄, 30 wt.% Al_2O_3 -70 wt.% SiO₂/ZrCl₄ and SiO₂/ZrCl₄, respectively

elevation to 573 K the intensity of all bands was decreased.

The results of 2-ethylpyridine adsorption (in the 1800–1200 cm^{-1} range) are presented in Fig. 5.

Al₂O₃

Several new IR bands appear in the spectrum after 2ethylpyridine adsorption on alumina: 3550, 3070, 2970, 2880, 1613, 1577, 1480, 1467 and 1440 cm⁻¹. Heating the sample up to 573 K reduced the intensity of all IR bands.

Al₂O₃/ZrCl₄

Upon adsorption of 2-ethylpyridine the following bands are present in the IR spectrum [Fig. 5(b), (e) and (f)]: 3065, 2970, 2940, 2880, 1620, 1600, 1480, 1460 and 1445 cm⁻¹. In spite of heating the sample at 573 K all bands remain in the spectrum.

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Fig. 4 Infrared absorption spectra of (a) Al_2O_3 , (b) $Al_2O_3/ZrCl_4$, (c) pyridine adsorbed and evacuated at 298 K on (a), (d) as for (c) after evacuation at 573 K, (e) pyridine adsorbed and evacuated at 298 K on (b), and (f) as for (e) after evacuation at 573 K

Electron Acceptor and Electron Donor Properties

The results of EPR after perylene and tetracyanoethene adsorption are presented in Table 2. Perylene adsorption on silica-alumina (70 wt.% SiO₂) as well as on ZrCl₄-treated alumina, silica-aluminas and silica resulted in the formation of surface paramagnetic species. The EPR spectra of the above samples had hyperfine structure identical to that observed for perylene cation radicals.^{19,25} The one-electron acceptor centres of these systems were able to withdraw one electron from the perylene molecule without the necessity of oxygen pre-adsorption. Alumina and silica-alumina with 87 wt.% Al₂O₃ content exhibit one-electron acceptor properties only if molecular oxygen is present on the surface. It was found that silica has no surface sites with one-electron acceptor properties. Only two of the four carriers used, *i.e.* Al_2O_3 and 87 wt.% Al_2O_3 -13 wt.% SiO_2 , possess one-electron donor sites. The introduction of ZrCl₄ causes these centres to disappear.



Fig. 5 Infrared absorption spectra of (a) Al_2O_3 , (b) $Al_2O_3/ZrCl_4$, (c), (d) 2-ethylpyridine adsorbed on (a) at 298 K after evacuation at 298 and 573 K, respectively, and (e), (f) 2-ethylpyridine adsorbed on (b) at 298 K after evacuation at 298 K and 573 K, respectively

Amount of Chlorine and Zirconium on the Surface

It was found that on the surface of $Al_2O_3/ZrCl_4$ catalysts there are 0.96 mmol g⁻¹ of chlorine ions and 0.42 mmol g⁻¹ of zirconium cations. 0.53 mmol g⁻¹ OH groups on alumina are calcined at 773 K.²⁶

Discussion

According to the definition, superacids should fulfil two criteria, *i.e.* an acid strength, H_0 , < -12 units and the ability to initiate *n*-alkane isomerization at low temperatures. In the case of the system under study it was impossible to perform direct measurements of acid strength. The catalyst became dark while in contact with benzene, the solvent for Hammett indicators, hence the colour change of the indicator was invisible. An indirect measure of the high acid strength of the Lewis centres was the ability of the sites in the Al₂O₃/ZrCl₄ system to withdraw one electron from a neutral molecule of

Table 2One-electron donor and acceptor properties of $ZrCl_4$ -based superacids (calcination temperature of carriers 773 K, $ZrCl_4$ evaporationtemperature 673 K)

	one-electron properties/ 10^{-15} spin g ⁻¹			
	acceptor			
catalyst	with O_2 preadsorption	without O_2 preadsorption	donor without O_2 preadsorption	
Al ₂ O ₃	125	0	425	
87 wt.% Al ₂ O ₃ -13 wt.% SiO ₂	156	0	104	
30 wt.% $Al_{2}O_{3} - 70$ wt.% SiO_{2}	988	114	0	
SiO,	0	0	0	
$Al_2O_3/ZrCl_4$	900	175	0	
$87 \text{ wt.\% Al}_{2}O_{3}-13 \text{ wt.\% SiO}_{2}/\text{ZrCl}_{4}$	650	156	0	
30 wt.% $Al_{2}O_{3}$ -70 wt.% $SiO_{2}/ZrCl_{4}$	1178	190	0	
SiO ₂ /ZrCl ₄	1900	250	0	

perylene in the absence of oxygen. We proved that superacid centres of the $Al_2O_3/AlCl_3$ system are also responsible for the perylene oxidation to cation radicals.⁸

Results of the reaction tests indicate the high catalytic activity of the acid centres which were able to initiate both *n*-butane and *n*-pentane transformations at low temperatures. Based on the above findings we could postulate that the alumina-zirconium tetrachloride system belongs to the solid superacids family. The superacid centres are formed as a result of $ZrCl_4$ reaction with the surface goups of alumina. The reaction could be followed by IR spectroscopy. The disappearance of IR adsorption bands ascribed to valence vibrations of the OH groups due to the $ZrCl_4$ effect indicates that the surface hydroxyls are at least one of surface centres that react with $ZrCl_4$ during superacid site formation. According to Peri²⁷ two types of hydroxyl group are present on the alumina surface: isolated and adjacent ones. Either could react with $ZrCl_4$:

Since the contribution of isolated hydroxyls amounts to 2-8% of all the hydroxyl groups present on alumina calcined at 773 K,²⁸ an excess of the reaction (1) product is expected. Both reactions proceed until all surface hydroxyls are used up and one can estimate the ratio of the Cl⁻ introduced onto the surface through reactions (1) and (2) to the number of OH groups on the untreated alumina. The Cl⁻/OH ratio should approach a value of 0.55-0.59. The observed ratio was 1.8 which is indicative of a large contribution from other reactions to the process of ZrCl₄ interaction with the surface. The introduction of ZrCl₄ onto alumina results in not only the disappearance of OH groups, but also the one-electron donor centres of Al_2O_3 being used up during catalyst preparation (Table 2). According to Flockhart *et al.*¹⁹ the adjacent surface oxygen anions formed during alumina calcination are responsible for the electron donor properties. Thus the third reaction of ZrCl₄ with alumina could be as follows:

$$Al - O - Al - O + ZrCl_4 \longrightarrow Al - O - Al - O \qquad (3)$$

The contribution of reaction (3) to the process of $ZrCl_4$ introduction on alumina can be evaluated. One can assume that the difference between the amount of Cl⁻ present at the surface and the amount introduced by reactions (1) and (2) is a measure of that produced by reaction (3). Using this assumption, we calculated the number of Zr^{4+} ions introduced by reactions (1), (2) and (3) and compared it with the number detected on the surface. The difference was *ca.* 12% which means that the model of surface reaction advanced describes satisfactorily the real catalyst formation. A similar model of Lewis acid interaction with alumina has already been suggested for the cases of AlCl₃⁸ and SbF₅.¹⁵ The surface centres (I), (II) and (III), having four-coordinated



Fig. 6 Variations of the quantity of ammonia adsorbed by Lewis (\bigcirc) and Brønsted (\bigtriangledown) acid centres of Al₂O₃/ZrCl₄ as a function of desorption temperature

 Zr^{4+} as well as electron-deficient Al^{3+} cations, should possess Lewis acid character. The results of IR measurements of ammonia (bands at 1600 and 1250 cm⁻¹) and pyridine (bands at 1610 and 1445 cm⁻¹) adsorption confirm the existence of the Lewis acid centres on the catalyst surface. On the other hand, the appearance of the adsorption band at 1410 cm⁻¹ for the adsorbed ammonia indicates that some Brønsted acid centres are also present. Pyridine adsorption, however, does not confirm the existence of Brønsted sites (the lack of a 1530 cm⁻¹ absorption band). Such an effect could be explained in terms of the basic strength of NH₃ and pyridine. The former is a stronger base (pK_{BH+} = 9) than the latter (pK_{BH+} = 5) and thus can react with centres of much lower acid strength.²⁹ Brønsted acid sites can be formed as a result of HCl adsorption on centres (I) and (II):

$$ZrCl_3^-H^+$$
 $ZrCl_4^-H^+$
O O O
Al-O-Al-O and Al-O-Al-O

Thermal desorption of ammonia performed in the IR cell allowed estimation of the stabilities of the NH_3 acid centre bonds which are a measure of acid strength. Variations of the quantity of NH_3 adsorbed by Lewis and Brønsted acid centres with desorption temperature are shown in Fig. 6.

Brønsted acid centres are weaker than the Lewis ones. Upon desorption at 423 K all ammonia which had been fixed as NH_4^+ is removed from the surface while *ca*. 50% of the originally coordinately bonded NH_3 still remains adsorbed. The strongest Lewis centres bonded ammonia at temperatures as high as 573 K. The results of pyridine and 2ethylpyridine adsorption confirm the existence of strong Lewis centres. It is known³⁰ that only strong Lewis acid sites can adsorb substituted pyridines. In Fig. 7, the results of the thermal desorption of pyridine and 2-ethylpyridine from the Lewis acid centres of the $Al_2O_3/ZrCl_4$ system are presented.

The shape of the adsorption curves indicates that on the surface of the system studied there are at least two kinds of Lewis acid centre: strong ones, which are responsible for both pyridine and 2-ethylpyridine adsorption (IR adsorption





Since silica and silica-alumna (30 wt.% Al₂O₃-70 wt.% SiO₂) have no one-electron donor centres, the reaction equivalent to reaction (3) will not proceed for these two supports. Since Lewis acid properties of the systems under study increase with the alumina content in the support, these centres may be formed with the participation of the alumina surface groups. The resulting centres of (I), (II) and (III) type may be considered as the acid sites for both alumina and silica-aluminasupported ZrCl₄. On the other hand, the presence of the Lewis acid and one-electron acceptor centres on the surface of the $SiO_2/ZrCl_4$ system indicates that zirconium cations in (IV) and (V) type centres cannot be excluded as a source of acid properties in the cases where silica and silica-aluminas were used as supports. Moreover, the hydrogen chloride formed during the reaction of ZrCl₄ with surface hydroxyls could modify sites (I), (II), (III), (IV) and (V), transforming them into secondary Brønsted centres.

Fig. 8 Relationship between surface properties and chemical composition of silica-aluminas: (a) Lewis $[(\bigcirc)$, pure carriers; (\bigcirc), after deposition of ZrCl₄] and Brønsted $[(\nabla)$, pure carriers, (\bigtriangledown) , after deposition of ZrCl₄] acidity. (b) Concentration of one-electron acceptor (with preadsorption of oxygen) (\blacksquare) and one-electron donor (\square) centres of pure carriers, and one electron acceptor centres (\triangle) after deposition of ZrCl₄



bands at 1610 and 1445 cm⁻¹), and weaker ones, which are able to fix only pyridine molecules. EPR measurements of perylene adsorption also confirm the existence of strong acceptor sites. They are able to withdraw an electron from a perylene molecule in the absence of pre-adsorbed oxygen, transferring it to a positively charged radical. Even such a strong acceptor as alumina needs oxygen to catalyse the electron transfer from perylene to the surface centre.¹⁹

The $Al_2O_3/ZrCl_4$ system catalyses the low-temperature isomerization of low alkanes as is the case for other known superacids. To check what kinds of surface centre are responsible for the superacid properties, the correlation between catalytic activity and concentration of different acid sites was studied. To this end, a set of silica-aluminas, 87 wt.% Al_2O_3 -13 wt.% SiO_2 and 30 wt.% Al_2O_3 -70 wt.% SiO₂ as well as silica, were chosen as ZrCl₄ carriers. The different surface properties of these solids, namely the different natures and concentrations of the sites for ZrCl₄ adsorption, allow preparation of catalysts which possess surface centres with predictable structures. Shown in Fig. 8 are the number of one-electron donor centres (which are potential substrates for ZrCl₄), as well as acid-base and one-electron acceptor sites of both supports and the resulting catalysts. The presented values represent the results of three independent measurements.

The $ZrCl_4$ introduced onto the support surface affects its properties. One can observe an increase in the number of both Lewis acid centres and weak one-electron acceptor sites, the appearance of strong one-electron acceptor centres, and the disappearance of both surface hydroxyls (see Fig. 2) and one-electron donor sites. The distribution of Brønsted centres was also affected by $ZrCl_4$, but the changes are irregular. The above findings indicate that reactions (1)–(3), typical of alumina, could take place, as well as reactions involving the surface OH groups originating from the silica:

 $\begin{array}{c} ZrCl_{3} \\ OH \\ -Si - + ZrCl_{4} \longrightarrow -Si - + HCl \\ (IV) \end{array}$ (4)



Comparison of the acid-base and one-electron acceptor properties of the catalyst studied with their ability to initiate *n*-pentane transformation at room temperature indicates that only the SiO₂/ZrCl₄ system was totally inactive. Hence, the Lewis acid centres of (IV) and (V) type, as well as secondary Brønsted sites resulting from their reaction with HCl, are too weak to initiate the *n*-alkane reaction. Note that, in spite of a high oxidizing strength, one-electron acceptor sites involving Zr⁴⁺ cations are incapable of starting the *n*-pentane to pentyl cation transformation.

The increase of alumina content in the $ZrCl_4$ support causes an increase of catalytic activity. From all the surface properties measured, the same trend was observed for the concentration of Lewis acid centres. For the pure alumina support, the rate of *n*-pentane reaction attains the highest value and the reaction of the less reactive *n*-butane becomes possible. This means that interaction of alumina with $ZrCl_4$ leads to the creation of superacid centres. If one assumes that the surface concentration of alumina is the same as in the bulk, it becomes possible to evaluate the number of Lewis acid centres of the surface alumina phase ($L_{Al_2O_3}$) on the basis of the following formula:

$L_{Al_2O_3} = L_{total} - L_{SiO_2} \times (share of SiO_2 in silica-alumina)$

where $L_{Al_2O_3}$ is the Lewis acidity of the alumina phase in the silica–alumina/ZrCl₄ system, L_{SiO_2} is the Lewis acidity of the SiO₂/ZrCl₄ system and L_{total} , the total Lewis acidity. There is good correlation between the Lewis acidity of the alumina phase with initial reaction rate of *n*-pentane isomerization. A similar correlation exists between the one-electron acceptor properties of the alumina phase (calculated as $L_{Al_2O_3}$) and the catalytic activity.

On the other hand, we have not observed any correlation between the Brønsted acid site concentration and the catalytic activity. This fact, together with the finding that the Brønsted acid sites are weaker than the Lewis ones, indicates that, for the $Al_2O_3/ZrCl_4$ system, acceptor centres are responsible for the superacid properties.

An analysis of the catalytic activity of the $Al_2O_3/ZrCl_4$ catalysts obtained on the basis of aluminas calcined at different temperatures (Fig. 9) allows the structure of the active superacid centres to be determined.



Fig. 9 Effect of carrier calcination temperature on initial reaction rate of *n*-pentane isomerization. Batch reactor, reaction temperature 333 K, *n*-pentane pressure 24.4 kPa, catalyst 1 g of $Al_2O_3/ZrCl_4$

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Surface properties of alumina strongly depend on the calcination temperature.^{19,20,27,28} Al₂O₃ calcined at 673 K possesses one-electron acceptor (surface Al³⁺ cations) and one-electron donor (OH groups) centres. With increasing calcination temperature up to 773 K, surface dehydration takes place resulting in an increase in the number of both oneelectron donor and one-electron acceptor centres, and in the appearance of isolated surface hydroxyls. Note that the origin of the one-electron donor properties changes from basic OH groups to surface O²⁻ anions.²⁰ Calcination at 873 K causes an increase in the number of one-electron donor and acceptor sites, as well as in the quantity of surface isolated OH groups. The latter value reaches the highest possible level. A further increase in the degassing temperature (to 973 K) results in an increase in the number of one-electron centres and a decrease of the concentration of the OH groups. Since for all the samples of alumina support, both OH groups and one-electron donor centres are found, reactions (1)-(3) could take place between $ZrCl_4$ and all of the aluminas studied. The type of acid centres formed depends of the calcination temperature of alumina. The centres (I) are formed on the surface of fully hydroxylated Al_2O_3 ($T_{calc} = 673$ K), while the number of (II) and (III) sites will increase with an increase in the alumina calcination temperature. The maximum observed for the catalytic activity at an alumina calcination temperature of 773 K proves that, for the formation of superacid centres, the presence of both O^{2-} anions (one-electron donor sites) and isolated OH groups is needed. This is an indication that these two surface groups participate in superacid Lewis centre formation. A possible mechanism for superacid site formation could be as follows:

$$\begin{array}{ccc} & ZrCl_3 & ZrCl_4 \\ OH & O & O \\ Al-O-Al-O-Al + 2 ZrCl_4 - Al-O-Al-O-Al + HCl \end{array}$$

There are two possible sources for the Lewis acidity of the above structure: aluminium and zirconium cations. Since the $ZrCl_4$ -treated silica does not possess any superacid active centres, in spite of the presence of $-(O)_2 - ZrCl_2$ and $-O - ZrCl_3$ surface groups, one can exclude Zr^{4+} cations as Lewis superacid centres. Hence, the surface-deshielded aluminum cation is the source of Lewis superacid properties. The positive charge of the Al^{3+} cation is enhanced by the electron acceptor effect of both the $ZrCl_4$ molecule adsorbed on the adjacent O^{2-} anion and $ZrCl_3$ species resulting from a $ZrCl_4$ reaction with the surface OH group. This site is able to initiate *n*-alkane isomerization. A possible mechanism involves attack of the centre on the electrons of the alkane C-H bond:

A similar mechanism for initiation of the *n*-pentane reaction has already been proposed for the $Al_2O_3/AlCl_3$ superacid system.¹⁶ The cation formed during the reaction undergoes further reactions. In the case of *n*-butane, the sole reaction is isomerizaton, followed by H⁻ recovery. When pentane is used as a substrate apart from isopentane, which is a product of pentyl carbocation isomerization, isobutane and small amounts of isohexanes were found among the reaction products. The latter compounds could result from decomposition of either the dimeric reaction intermediate³¹ or alkyl chains irreversibly fixed to the Lewis sites.¹⁸ The latter

$$\begin{bmatrix} CH_{3}CH_{2}CH_{2}CH_{2}CH_{2} \\ \downarrow \end{bmatrix}^{+} \longrightarrow H^{+} + CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2} \\ \downarrow \downarrow L \end{bmatrix}$$

L-R species could react with the carbocations present in the system to form longer alkyl chains which would decompose to yield highly stable isobutane and higher alkanes in minor amounts.¹⁸

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