

Superacid properties of $\text{Al}_2\text{O}_3\text{-SbF}_5$ catalytic system

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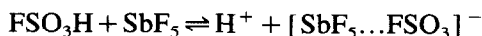
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Abstract

Chemical and catalytic properties of $\text{Al}_2\text{O}_3\text{-SbF}_5$ system has been studied. It was found that alumina upon SbF_5 adsorption became solid superacid of Brønsted nature, able to catalyze n-pentane low temperature isomerization. The following structure of superacid active center has been postulated: $[\text{=Al-O-SbF}_5]^- \text{H}^+$. The stability of this catalyst was evaluated using time-on-stream theory of catalysts decay and then compared with other Brønsted ($\text{Al}_2\text{O}_3\text{-BF}_3$) and Lewis ($\text{Al}_2\text{O}_3\text{-AlCl}_3$) superacid systems. It was found that Brønsted superacid centers are more stable than Lewis ones.

1. Introduction

Acid strength of pure sulphuric acid ($H_0 = -11.4$) is conventionally considered as a limit of the strength of typical acids. The systems which are characterized by higher value of acid strength ($H_0 < -11.4$) are classified as superacids [1,2]. Superacids possess interesting catalytic properties. They catalyze ionic, low temperature transformations of such weak bases like low alkanes. For example, solutions of SbF_5 with protonic acids like HF or FSO_3H with acid strength in H_0 scale lower than -20.5 and -19.5 , respectively, are able to protonate methane and thus initiate its alkylation [2–5]. High acidity of the superacids is connected with the equilibrium of reaction between SbF_5 and conjugated base of the protonic acid:



which due to the acceptor nature of SbF_5 is shifted to the right. The resulting complex anion, being a

soft base, is not able to fix strongly proton which thus gains the activity responsible for superacid properties of the solution.

Antimony pentafluoride reacts also with solids like: alumina, silica, silica–alumina, titania, silica–titania system [6], zeolites [7,8], tin and magnesium oxides [7] and graphite [9] with solid superacid formation. In the presence of these systems n-alkanes like butane or pentane isomerize at room temperature [6–8]. The general theory of solid superacid action, contrary to the case of superacid solutions, has not yet been developed.

The most investigated SbF_5 based solid superacid is the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-SbF}_5$ system. However, in spite of much work, the problem of structure of the superacid active center is still to be solved. Hattori [7] proposed that aluminium cations adjacent to adsorbed SbF_5 might be considered as active Lewis superacid centers [7]. On the other hand, Taniguchi [10] reported that Brønsted acid sites of $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-SbF}_5$ system possess higher acid strength than Lewis ones, and they should be responsible for superacid properties of the system.

Solid superacids are not stable and undergo deactivation during the reactions. Catalytic activity is then a function of two factors: acidity and stability of surface sites. To define the stability of the active centers it is necessary to study the kinetics of catalyst deactivation.

A number of theories describe the kinetics of catalyst decay. One of the most general is the time-on-stream theory developed by Wojciechowski [11]. The principal assumption of the theory is that the fraction of the active centers (Θ) left unpoisoned at time t is given by:

$$\Theta = S/S_0 = (1 + Gt)^{-M} \quad (1)$$

where S is the concentration of active centers after reaction time t , S_0 is the initial concentration of active centers, G and M are decay parameters

The kinetic equation of an elementary reaction step can be always expressed as:

$$d[A]/d\tau = kS^n[A]^a \quad (2)$$

where $[A]$ is the substrate concentration, n is the reaction order towards surface centers, a is the reaction order towards substrate, k is the rate constant, τ is the contact time.

Substituting for S in Eq. 1

$$d[A]/d\tau = kS_0^n(1 + Gt)^{-N}[A]^a \quad (3)$$

where $N = nM$

It is evident that the reaction rate is a function not only of substrate concentration but also of the deactivation parameters N and G . According to time-on-stream theory all catalytic systems can be classified into three classes [11,12]. Class I, $N > 1$, are slowly aging catalysts, Class II, $N = 1$, exhibit limiting deactivation whereas Class III, $N > 1$, are rapidly aging catalysts. Lewis superacids like $Al_2O_3/AlCl_3$ belong to the last group of catalysts with $N = 2$ [13].

In our previous works we found that Lewis acids like boron trifluoride and aluminum chloride react with alumina forming Brønsted and Lewis acid superacid centers, respectively [13,14]. The aim this paper is to extend the study on the $SbF_5-Al_2O_3$ system to compare structure, nature, stability and catalytic properties of the superacid sites

with that of BF_3 -Alumina (Brønsted) and $AlCl_3$ -Alumina (Lewis) systems.

2. Experimental

1 g of γ -alumina (Pierce Inorganics), grain diameter 0.5–1.0 mm, was placed in a glass batch reactor (74 ml) and then calcined in vacuo ($1.3 \times 10^{-2} \text{ Nm}^{-2}$) for 3 h at 773 K. On cooling (293 or 373 K) the sample was contacted for 10 min. with SbF_5 (Ventron) under the pressure equal to SbF_5 saturated vapor pressure at 293 K. After evacuation of unreacted SbF_5 , n-pentane as a vapor ($26.8 \times 10^3 \text{ Nm}^{-2}$) was introduced into the reactor. In some experiments SiO_2 (Pierce Inorganics) was used as the SbF_5 support. The results obtained from batch reactor experiments were approximated using a least squares fit by the function:

$$x = a \tanh(b \times t) \quad (4)$$

where x denotes pentane mole conversion, t is the reaction time, a and b are fitting parameters, which was used for reaction rate calculations. The initial rate of pentane reaction (i.e., that calculated using Eqs. 4 and 5 for zero contact time) was assumed to be a measure of catalytic activity.

The analyses of reaction products were made on a gas chromatograph fitted with a squalane capillary column (50 m).

IR spectra were recorded at room temperature using a Specord IR-75 spectrophotometer. For IR measurements alumina samples were pressed into thin, ca. 10 mg cm^{-2} wafers. The wafer was placed in a vacuum cell and burned at 773 K in the stream of air. After 1 h the cell was outgassed in vacuo to $1.3 \times 10^{-2} \text{ Nm}^{-2}$ and the desorption of gases was continued for additional 2 h. Upon recording the IR spectrum of the sample at room temperature (293 K) SbF_5 vapors were admitted into the cell (pressure equal to saturated vapor pressure of SbF_5 at 293 K). The exposure time was 10 min. The IR spectra of pretreated samples were recorded upon evacuation of the cell. The sample was then exposed to the vapors of pyridine,

the partial pressure being equal to the saturated vapor pressure at 293 K. After 10 min exposure the cell was reevacuated and the IR spectrum was recorded. Pyridine was subsequently desorbed at different temperatures i.e. at 373, 473 and 573 K, and the IR spectra of the respective samples were recorded.

Flockhart et al. [15,16] proved that perylene and tetracyanoethylene adsorption can be used as a measure of one-electron acceptor and one-electron donor properties of the catalysts, respectively. Samples of catalysts placed in tubes under dry, deoxidized nitrogen were covered with benzene solution (0.01 mol dm^{-3}) of either perylene or tetracyanoethylene, cooled to 77 K and sealed under reduced pressure. Measurements of the number of ion-radicals formed were carried out using ESR JEOL 3x spectrometer.

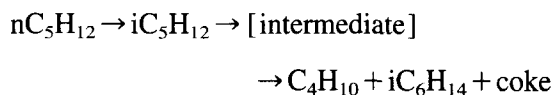
3. Results

SbF_5 treated alumina catalyzes n-pentane transformation at temperature as low as 293 K. Methylbutane, methylpropane and small amounts of methylpentanes were identified as reaction products. Typical results of the reaction are presented in Fig. 1.

The morphology of product conversion vs. total conversion curves indicates that methylbutane is a primary reaction product (Fig. 1A). The other

products i.e. methylpropane and methylpentanes are formed from methylbutane in consecutive reactions. It is better seen when methylbutane was taken as the reaction substrate (Fig. 2B). It can be also seen that methylpropane is rather the secondary than the primary product of methylbutane reaction.

Pentane total conversion attains stable value of $\approx 45\%$ after 35 min of the reaction, the value being much lower than equilibrium pentane conversion at 293 K (x_{eq} close to 100%). It may be explained by deactivation of the superacid caused by coke formation. The complete scheme of pentane reaction can be written as follows:



According to Hattori [7] the methylbutane dimer can be regarded as the intermediate product of the reaction.

To describe the catalyst stability phenomena it is convenient to develop a kinetics equation which includes terms describing the change of the concentration of active centers with time-on-stream. Such an equation for pentane isomerization in the presence of $\text{Al}_2\text{O}_3\text{-AlCl}_3$ Lewis superacid has been already proposed [13].

Reaction of pentane catalyzed by $\text{Al}_2\text{O}_3\text{-SbF}_5$ superacid system is of consecutive character. Since pentane conversion into methylbutane and

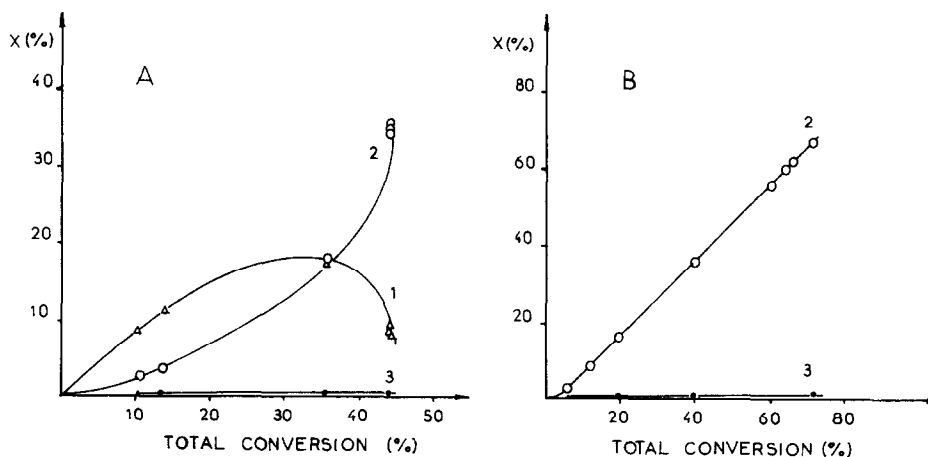


Fig. 1. Pentane (A)/isopentane (B) conversion into methylbutane (1), methylpropane (2) and methylpentanes (3) vs. pentane total conversion. Batch reactor, reaction temperature 293 K, pentane pressure $26.8 \times 10^3 \text{ Nm}^{-2}$.

Table 1
Rate equations for pentane isomerization reaction

Rate equation	Rate limiting step
$r = \frac{k_1 S_0 p_0 (1-x)}{1 + (K_{II}/K_I + K_{III}) p_0 x}$	pentane adsorption
$r = \frac{k_2 S_0 K_I (1-x)}{1 + K_I p_0 (1-x) + K_{III} p_0 x}$	pentane surface isomerization
$r = \frac{k_3 S_0 K_I K_{II} p_0 (1-x)}{1 + K_I (1 + K_{II}) p_0 (1-x)}$	pentane desorption

K_I , K_{II} , K_{III} equilibrium constants of pentane adsorption, surface isomerization and desorption, respectively.

k_1 , k_2 , k_3 rate constants of pentane adsorption, isomerization and desorption, respectively.

x pentane total conversion.

p_0 pentane initial pressure.

S_0 initial concentration of active centers.

methylpropane is lower than that of methylbutane into methylpropane (see Fig. 1) one can conclude that rate determining step is rather connected with pentane isomerization step and not with dimer formation or its decomposition. In such a case one can use the total pentane conversion (to methylbutane and methylpropane) to develop the kinetic equation of pentane isomerization. Using the Langmuir–Hinshelwood formalism three rate expressions can be written depending on whether pentane adsorption, surface isomerization of pentyl cation or methylbutane desorption is the rate limiting step. Equations obtained are listed in Table 1.

All equations are of a similar form:

$$r = A(1-x)/B + Cx$$

Depending on reaction mechanism parameter B can equal 1 (pentane adsorption is the rate determining step) or its value can be higher than 1 (surface reaction or product desorption control the rate of pentane isomerization).

The substitution of S_0 in equations listed in Table 1 by S calculated from Eq. 1 leads to the general expression:

$$r = A(1-x)/(B + Cx)(1 + Gt)^N \quad (5)$$

The experimental data i.e. r (calculated using Eq. 4), x , and t were fitted to Eq. 5 and the least square estimates of all parameters were deter-

mined using the minimum sum of square residuals as the criterion of fit. Calculated parameters for pentane reaction at 293 K in the presence of the Al_2O_3 – SbF_5 superacid are listed in Table 2.

The parameter B was close to unity which indicates that pentane adsorption with carbocation formation is the rate determining step of pentane isomerization (see Table 1). The value of N which was found to be higher than 1 allows us to classify the superacid system to the third class of catalyst decay.

The parameter A , equal to initial reaction rate, can be regarded as a measure of catalytic activity that is independent of catalyst decay.

The activity of catalysts under study depends on the conditions both of catalyst synthesis and pentane reaction (Table 3). The results indicate that SbF_5 interaction with all carriers studied leads to the ability of the catalysts to initiate n-pentane transformations at room temperature (293 K). Catalytic activity depends on temperature of SbF_5 with support reaction. With the rise of the temperature the initial reaction rate of pentane trans-

Table 2
Kinetic constants of n-pentane isomerization reaction. Reaction rate: $r = A(1-x)/(B + Cx)(1 + Gt)^N$. Catalyst: Al_2O_3 – SbF_5 (0.05 g), reaction temperature: 293 K

A	B	C	G	N
0.0297	1.0210	0.0360	0.0268	1.1462

Table 3
Catalytic properties of support– SbF_5 superacid systems. Reaction temperature 293 K, pentane partial pressure 26.8×10^3 Nm⁻²

SbF ₅ carrier	Temperature		Initial reaction rate (g ⁻¹ min ⁻¹)
	of catalyst synthesis (K)	of pentane reaction (K)	
Al ₂ O ₃	273	273	0.174
	293	293	0.594
	373	273	0.069
	373	293	0.275
	373	333	1.247
	373	373	0.776
SiO ₂	293	293	1.340

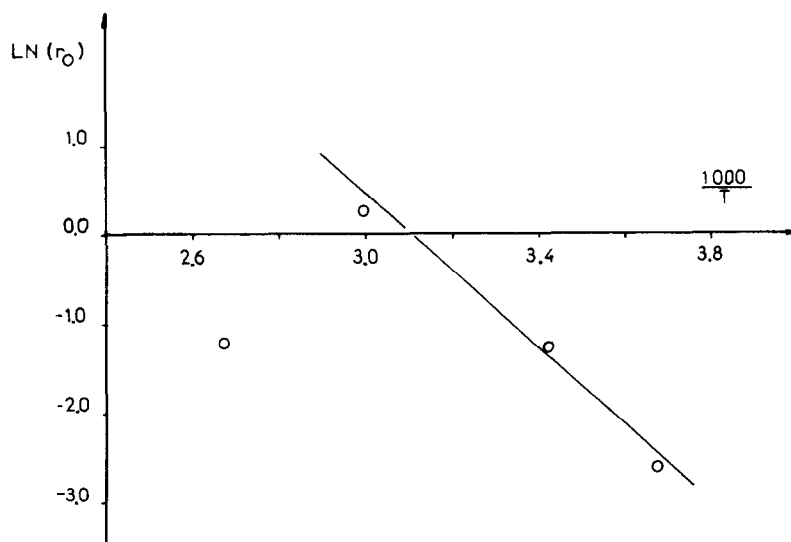


Fig. 2. Arrhenius plot for pentane isomerization in the presence of $\text{Al}_2\text{O}_3\text{-SbF}_5$ catalyst.

formation diminishes. For $\text{Al}_2\text{O}_3\text{-SbF}_5$ catalysts the dependence of reaction rate on reaction temperature was also studied. In the temperature range 273–333 K the initial reaction rate obeys the Arrhenius law ($E_a = 9 \text{ kcal mol}^{-1}$). Further rise of temperature resulted in decrease of the initial reaction rate (Fig. 2).

The results of IR measurements are presented in Figs. 3 and 4. Two absorption bands with maxima at 3730 and 3670 cm^{-1} characteristic of surface OH groups were observed for alumina (Fig. 3, curve 1). As a result of the interaction of SbF_5 with the alumina surface the bands at 3800–3600 cm^{-1} typical of pure alumina disappear and new

bands with maxima at 3550 and 1640 cm^{-1} develop (Fig. 3, curve 2).

Pyridine adsorption on $\text{Al}_2\text{O}_3\text{-SbF}_5$ system results in appearance in lower wave range of the IR spectrum of new absorption bands with maxima at 1533 and 1460 cm^{-1} typical for the interactions with Brønsted and Lewis acid centers respectively [17]. The intensities of these bands as a function of desorption temperature are presented in Fig. 4.

One-electron acceptor and one-electron donor properties of the systems under study are gathered in Table 4. All catalysts possess acceptor centers able to transform perylene molecule into corre-

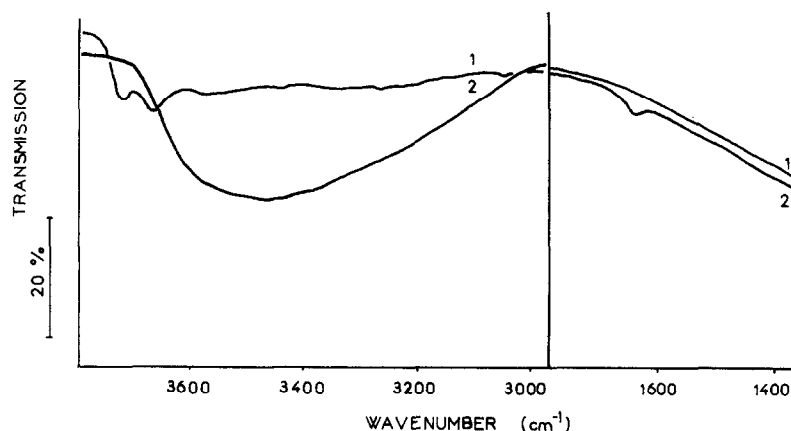


Fig. 3. IR absorption spectra of: (1) Al_2O_3 , (2) pyridine adsorbed on Al_2O_3 , (3) $\text{Al}_2\text{O}_3 + \text{SbF}_5$, pyridine adsorbed on (3) at 293 K after evacuation at: (4) 293 K, (5) 573 K.

Table 4
One-electron properties of superacid systems of carrier-SbF₅ type

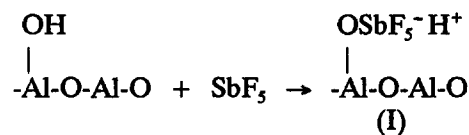
Catalyst	One-electron sites (spin/g × 10 ⁻¹⁵)	
	Acceptor	Donor
Al ₂ O ₃	0	425
Al ₂ O ₃ -SbF ₅	165	0
SiO ₂	0	0
SiO ₂ -SbF ₅	92	0

sponding cation radical. Introduction of antimony pentafluoride onto alumina causes the disappearance of one-electron donor properties of the carrier.

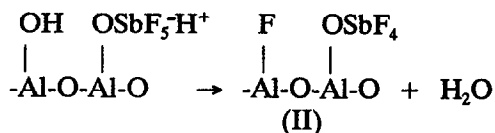
4. Discussion

The high acid strength of the alumina-SbF₅ system, higher than that of pure sulfuric acid [6], as well as the ability to catalyze n-pentane low temperature transformation allow us to classify it as a superacid. IR measurements performed during the synthesis of the catalyst as well as measurements of one-electron properties of alumina before and after SbF₅ adsorption give information on SbF₅ interactions with Al₂O₃ surface sites.

The disappearance of the IR absorption bands in the range 3800–3600 cm⁻¹ assigned to valence vibrations of surface hydroxyl groups [18] indicates that they react with SbF₅:

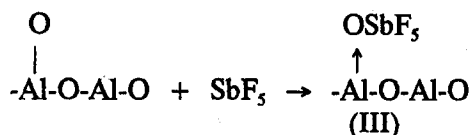


The resulting surface group (I) could be regarded as the SbF₅-HF superacid fixed to alumina. The broad IR band observed at 3400–3000 cm⁻¹ indicates that the proton from the -OSbF₅⁻H⁺ group could interact with lattice oxygen anions of alumina with hydrogen bond formation [19]. The group (I), according to Tanabe [7] could undergo further reaction with adjacent OH group:



The reaction results in the surface fluorination accompanied by water formation. The appearance of the band at 1640 cm⁻¹ characteristic for water molecule, confirms the possibility of surface fluoride formation.

The disappearance of one-electron donor centers upon SbF₅ adsorption on alumina indicates that these sites participate in the reaction. One-electron donor properties of alumina calcined at 773 K are assigned to exposed oxygen anions [16]. Hence, SbF₅ similarly as other Lewis acids, like AlCl₃ or BF₃ [14,20], could be coordinatively bonded by donor oxygens of alumina:



The adsorption of a strong electron acceptor like SbF₅ affects the charge distribution on adjacent atoms. The electron deficit on the Al³⁺ cation increases, which is equivalent to an increase of the electron acceptor properties of the system. The results of perylene adsorption (see Table 4) confirm that introduction of SbF₅ onto alumina surface results in the formation of strong one-electron acceptor centers. These sites, non-existent on alumina itself are able to withdraw one electron from perylene molecule in the absence of preadsorbed oxygen, the catalyst of electron transfer.

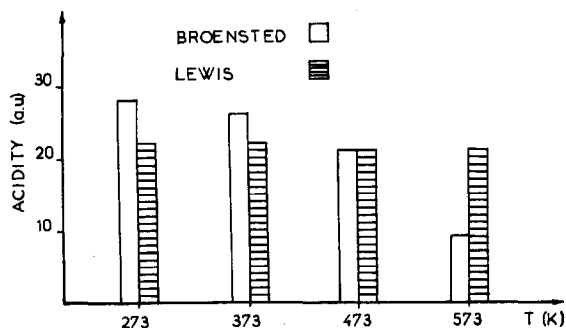


Fig. 4. Acid centres of Al₂O₃-SbF₅ catalysts.

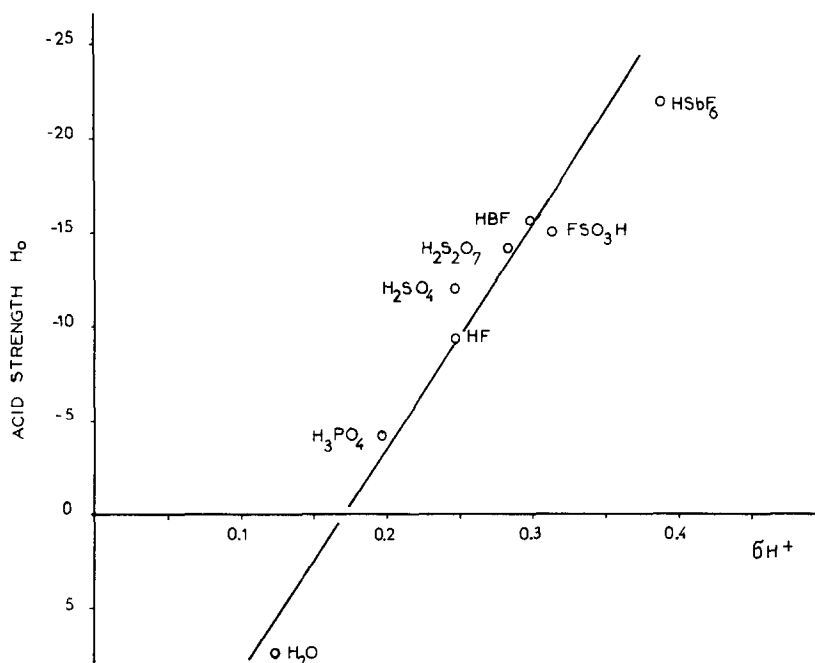


Fig. 5. Correlation between acid strength (H_0) of some typical Brønsted acids and the values of proton partial charges.

The nature of the centers formed as a result of alumina with SbF_5 reaction can be studied by IR examination of probe molecules adsorption. Pyridine was selected for the study of the acid properties of the catalyst. Observed bands with maxima at 1533 and 1430 cm^{-1} of adsorbed pyridine characteristic for Brønsted sites and Lewis centers interactions with probe molecule respectively [17]. Both types of centers possess high acid strength since evacuation performed at temperatures as high as 573 K does not cause desorption of the adsorbed base (Fig. 4).

More information concerning the structure of active superacid centers could be obtained when carriers other than alumina but with known sur-

face groups are used as SbF_5 support. Silica with non-acidic and non-basic OH groups and lattice oxygens was chosen.

One can predict that in the case of silica support, SbF_5 will form Brønsted acid sites of the $-SbF_5^- H^+$ type (structure I). The absence of donor sites of the alumina phase makes formation of Lewis acid centers of structure III impossible.

The results of the catalytic test indicates that SbF_5 adsorption on alumina and silica supports leads to formation of superacid sites. It means that superacid properties could originate from reaction of SbF_5 with centers of both alumina and silica phases. The action of SbF_5 is then different from that of $AlCl_3$ [20] or BF_3 [14] since the latter

Table 5
Model centers of solid Brønsted superacids

No.	Superacid			Model of catalytic site	Partial charge on H^+ [a.u.]
	Support	Calc. Temp. (K)	Lewis acid		
1	Al_2O_3	773	SbF_5	$SbF_5 \cdot O=Al-O-SbF_5^- H^+$	0.323
2	Al_2O_3	773	BF_3	$BF_3 \cdot O=Al-O-BF_3^- H^+$	0.221
3	Al_2O_3	573	BF_3	$O=Al-O-BF_3^- H^+$	0.171
4	SiO_2	773	SbF_5	$SbF_5 \cdot O=Si-(O)_2-SbF_5^- H^+$	0.338
5	Al_2O_3	773	$AlCl_3$	$AlCl_3 \cdot O=Al-O-AlCl_3^- H^+$	0.073

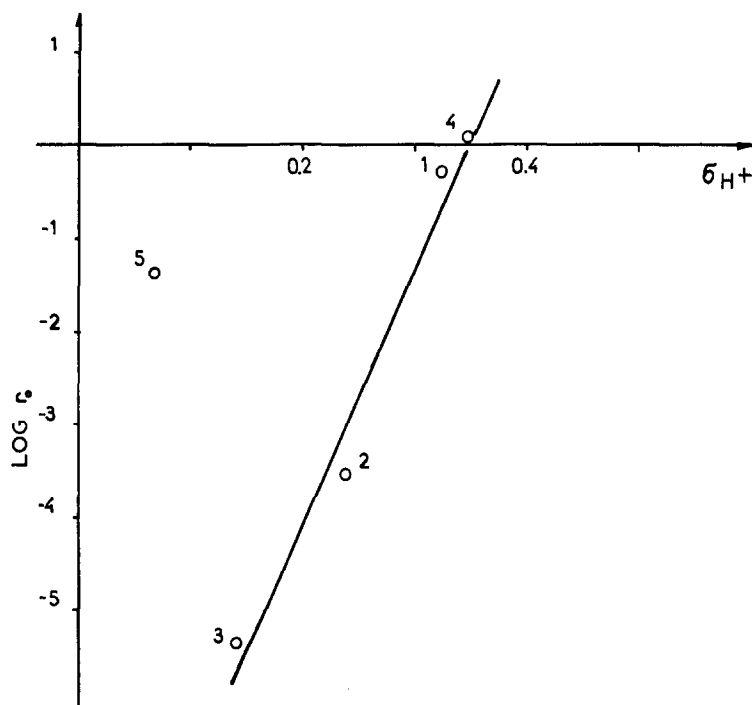


Fig. 6. Dependence of pentane initial reaction rate on acid strength of the active superacid centers proposed in Table 5.

compounds form superacid sites in reactions with surface centers of alumina phase only. The following surface groups can be thus considered as potential superacid centers:

Al- or Si-bonded $[-O-SbF_5^-]H^+$ group (structure I); Al^{3+} of structure III; Sb^{5+} from Al- or Si-bonded group $-O-SbF_4$ (structure II).

Centers of structure I are Brønsted acid sites while the other ones are of acid Lewis nature. To check which of these two types of acid sites can be responsible for superacid properties, the changes in superacid activity with temperature were examined. According to Tanabe [7] the catalytic system $Al_2O_3-SbF_5$ is not stable. With rise in temperature the Brønsted centers of structure I undergo transformation with non-acid sites of structure II formation. Our results (see Table 3) confirm that the catalysts obtained at higher temperature are less active and possess less Brønsted superacid centers (see Fig. 4) than those formed at lower temperature. This phenomenon can be considered as a premise indicating that Brønsted acid centers are responsible for the superacid properties of the catalysts under study.

Acid strength measurements of solid superacids are difficult to perform. It is however possible to evaluate acid strength on the basis of the distribution of partial charges in the idealized superacid center. Positive charge localized on proton can be regarded as a measure of the acid strength of a Brønsted acid; the higher the value of the charge, the higher the acid strength of an acid. It is illustrated by Fig. 5, where correlation between acid strengths of some typical Brønsted acids and the values of partial charge localized on their protons is presented. The calculation of charge distribution were performed according to Sanderson method [21] which is based on the electronegativity equalization principle. The linear correlation observed confirms the assumption that proton charge can be taken as a reliable measure of the acid strength of protonic acids.

Superacid centers of the systems under study can be approximated by the following model species (Table 5); The model sites results from SbF_5 reaction with the hypothetical molecules $O=Al-OH$ and $O=Si(OH)_2$ which idealize alumina and silica surface groups, respectively. SbF_5 can react

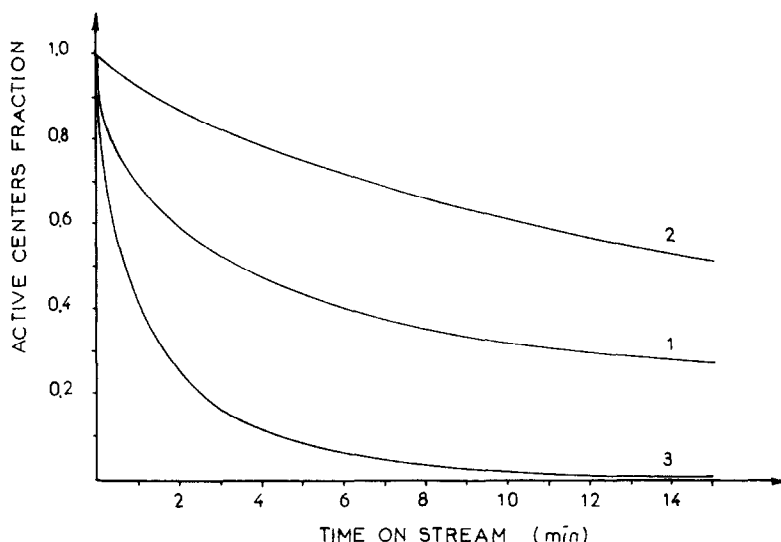


Fig. 7. Change of active centers fraction with reaction time for (1) Al₂O₃-SbF₅, (2) Al₂O₃-BF₃ and (3) Al₂O₃-AlCl₃.

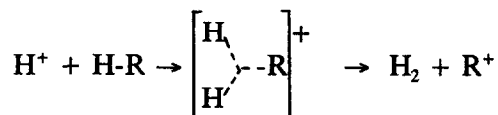
with both hydroxyl group and oxygen. It reflects the real situation when Lewis acid reacts with OH groups and electron donor oxygens of a support. SbF₅ possesses such strong acceptor properties that it is able to react not only with electron donor oxygens of alumina but also with oxygens originating from SiO₂ lattice which cannot be regarded as donor sites.

BF₃ is able to react with both the OH group and the oxygen of O=Al-OH forming a model of the alumina-BF₃ system, when the carrier has been calcined at 773 K [14]. If the calcination temperature is low (573 K) surface hydroxyls are the only sites accessible, then BF₃ could react only with them and the species [O=Al-O-BF₃]⁻H⁺ represents this particular catalytic system.

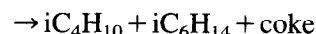
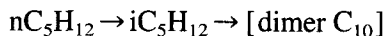
Table 5 also includes species which can be regarded as an approximation of the Brønsted acid center of the Al₂O₃-AlCl₃ system [13,20]. For all model superacid sites, the positive charge localized on the protons was calculated. The linear correlation between proton charge and the logarithm of the initial reaction rate of pentane reaction (Fig. 6) was found for two catalytic systems, i.e. those based on the BF₃ and SbF₅ reactions with supports. Since alumina-BF₃ superacid is of Brønsted nature [14] then for SbF₅ containing superacids Brønsted centers should also be responsible for superacid properties. In the case

of the Al₂O₃-AlCl₃ system, the experimental results do not fit the obtained correlation. The acidity of the model center AlCl₃·O=Al-O-AlCl₃ H⁺ seems to be too low to explain the high catalytic activity of the system. It is in agreement with our previous works [13,20] where we postulated that just Lewis and not Brønsted acid sites of Al₂O₃-AlCl₃ catalyst are responsible for superacid properties of the system.

On the basis of the above considerations one can conclude that Al₂O₃-SbF₅ is a Brønsted type superacid. n-Pentane reaction then starts from proton attack on electrons of the C-H σ bond with pentacoordinated carbonium ion formation:



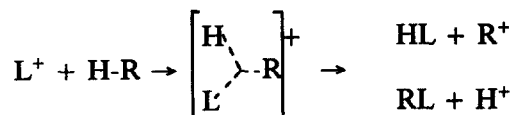
which decomposes to form pentyl carbenium cation. The latter undergoes isomerization leading to methylbutane, the intermediate reaction product.



The next reaction step is the dimerization of methylbutane which is followed by dimer cracking with methylpropane, to form the main reaction product [22]. The other products of dimer decom-

position are methylpentanes, observed in small quantities, and coke which remains adsorbed on the surface [22]. It is this coke formation which is the reason for catalyst decay.

It is interesting to compare the action of Brønsted superacid with that of Lewis nature for example $\text{Al}_2\text{O}_3\text{-AlCl}_3$. For the latter, the reaction starts from Lewis site attack on C–H bond of pentane molecule [13]:



The resulting surface non-classical cation can decompose in two directions:

- (1) with pentyl cation formation, which isomerizes to methylbutane;
- (2) with alkyl chain attached to the active center formation.

The second reaction diminishes the number of superacid active sites and thus is responsible for catalyst decay. Since the mechanisms of the deactivation the Brønsted and the Lewis superacids are different it should be reflected in their stability. In the case of Brønsted superacids the active centers are blocked by coke: the final, heavy product of consecutive reactions. On the other hand, Lewis superacid sites can be eliminated during each active transition-state decomposition. The latter mechanism seems to be more effective, so one can predict that Lewis superacids should be less stable than Brønsted ones.

It is possible to calculate, using Eq. 1, the change in the fraction (Θ) of active centers with reaction time. This is illustrated in Fig. 7 where data obtained for $\text{Al}_2\text{O}_3\text{-AlCl}_3$ and $\text{Al}_2\text{O}_3\text{-BF}_3$ superacid systems are also presented [13,14].

The number of unpoisoned active centers diminishes with time-on-stream, with the rate depending on their nature. Superacid Brønsted sites ($\text{Al}_2\text{O}_3\text{-SbF}_5$ and $\text{Al}_2\text{O}_3\text{-BF}_3$) are much

more stable than Lewis ones ($\text{Al}_2\text{O}_3/\text{AlCl}_3$) which is consistent with two different mechanisms proposed for active site decay for these two classes of acid centers. It may also explain the lack of catalytic activity of Lewis superacids sometimes observed. The rate of deactivation of these systems is so high that in spite of their great initial activity they could rather act as reagents than as catalysts.

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