PREPARATION OF SOLID SUPERACID CATALYSTS BY CHEMICAL MODIFICATION OF OXIDES. I

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Properties of solid acid catalysts prepared by modification of oxides have been examined. The oxides Al_2O_3, SiO_2, TiO_2, SnO_2, Sb_2O_3, ZrO_2 and $ZrSiO_4$ were impregnated by aqueous solutions of H_2SO_4, H_3PO_4, NH_4F and NH_4Cl, respectively, and calcined at 500, 650 and 800°C. For the so prepared catalysts, the strength and number of their acid centres and their activity for hydrocarbon reactions were determined.

The acid systems, which have the strength of the acid sites lower than $H_0 = -12$ and which are capable of catalyzing transformations of alkenes already at temperatures below 100°C are commonly called superacids. Examples of such systems are e.g. $SbF_3/HOSO_3F$, SbF_5/HF, BF_3/HF and $AlCl_3/HCl$ (refs[1-4]). Superacidic properties can be observed also for some oxides such as e.g. Al_2O_3, SiO_2, Al_2O_3/SiO_2 and SiO_2/TiO_2 modified by SbF_5 (ref.[5]), alumina modified by protic inorganic[6-8] and Lewis acids[5,9,10], by halogens and their organic compounds[11,12], ZrO_2, SnO_2 and TiO_2 modified by H_2SO_4 (refs[13-17]), silicas modified by some Lewis acids[18,19] or halogens[20], etc.

The aim of this work was to compare acidic and catalytic properties of Al_2O_3, SiO_2, TiO_2, SnO_2, Sb_2O_3, ZrO_2 and $ZrSiO_4$ modified by aqueous solutions of H_2SO_4, H_3PO_4, NH_4F and NH_4Cl.

EXPERIMENTAL

Compounds used. Antimony trioxide (Merck, pure, surface area 0·8 m^2/g), tin dioxide (pure, surface area 4·1 m^2/g), aluminium oxide (γ-alumina from aluminium chloride, sample No. 86 02 181, obtained from Chemical Works Litvínov, surface area 212 m^2/g), silicon dioxide (silica gel, Koch–Light Laboratories, surface area 600 m^2/g), titanium dioxide (as rutile, obtained from Chemical Works Přerov, surface area 9 m^2/g), zirconium silicate (ZrO_2SiO_2), of unknown structure (obtained from Ceramic Works Rakovník, surface area 0·1 m^2/g), zirconium dioxide — black modification (Ventron 98% purity, surface area 0·19 m^2/g) and white modification (Ventron, 99% purity, surface area 4·5 m^2/g), ammonium fluoride (Lachema, per analysis), ammonium chloride (Lachema, pure), phosphoric acid 85% (Lachema, pure), sulphuric acid

98% (Lachema, chemical purity grade), benzene (Lachema, per analysis, distilled and dried over sodium), cyclohexene (Fluka, pure, distilled and dried over sodium),n-hexane and p-xylene (both Reachim, pure, distilled and dried over sodium), pyridine (Lachema, technical purity grade, redistilled and dried with NaOH), nitrogen (Technoplyn, dried by molecular sieve).

Catalyst preparation. The dried oxide (105°C, 2 h) was impregnated by an excess of 1 mol/l aqueous solution of the modification agent (H_2SO_4, H_3PO_4, NH_4F or NH_4Cl). The suspension so formed was heated to about 95°C for 4 h with intermittent stirring. After cooling and decantation, the samples were separated by filtration with suction, dried without washing at 150°C under vacuum (c. 65 kPa) for 2 h and then calcined in a quartz tube reactor in a stream of nitrogen at 500, 650 or 800°C. The prepared samples were stored sealed in glass ampoules.

Maximum strength of acid centres. The maximum strength of acid centres of prepared catalysts was determined by the indicator method[24]. For measuring the strength of acid centres within the H_0 range -3 to $-14\cdot52$, the following colour acid-base indicators were used: dicinnamalacetone ($H_0 = -3$), benzalacetophenone ($H_0 = -5\cdot6$), antraquinone ($H_0 = -8\cdot2$), p-nitrochlorobenzene ($H_0 = -12\cdot7$), m-nitrochlorobenzene ($H_0 = -13\cdot16$), 2,4-dinitrotoluene ($H_0 = -14\cdot52$).

Number of acid centres. The number of surface acid centres was estimated on the basis of the weight determination of the amount of chemisorbed bases. The sorbates used were pyridine and benzene. These substances differ significantly in their basicity. One can thus assume that the strong base pyridine chemisorbs on nearly all acid centres while the weak base benzene occupies only strong acid centres (c. from $H_0 < -5\cdot6$). Determination of the acid centres on the surfaces of solid substances is known to be ladden with an error caused e.g. by the invalidity of the assumption that one molecule of the base is chemisorbed on one acid centre or that the bases can be bonded to the solid surface also by other than by acid-base interactions. However, it seems likely that the catalysts prepared in this work have comparable surface properties. With regard to the fact that for further discussion only relative data are needed, the sorption method can be taken as relevant for this purpose.

Determination of base sorption. To c. 1 g of the sample placed in a glass tube reactor, 0·2 ml of the dry sorbate (pyridine of benzene) were added and the reactor was thightly sealed. After 30 min for equilibrium establishment, the sorbate bonded physically was desorbed by stream of nitrogen (50 ml/min flow rate) for 2 h at 50°C. The amount of chemisorbed compound was measured by weighing. The amount of pyridine sorbed on all the samples was taken as the total number of acid centres and the amount of sorbed benzene was taken as the number of strong acid centres present on the surface of these catalysts.

Type of acid centres. The type of acid centres (protic or aprotic ones) was estimated from the position of IR absorption bands of the chemisorbed pyridine. The assignment of individual absorption bands was made on the basis of reported data[21-23]. IR measurements were carried out on Perkin–Elmer 1750 FTIR spectrometer, using the diffusion method. For this purpose, the samples used in determination of pyridine sorption were taken to IR measurements.

Catalytic activity. The aim of catalytic activity measurements was to verify the results of measurements of acid strength by colour indicators. We used three hydrocarbons as reactants which are known to undergo reactions (isomerization, cracking) on the centres of different acidity. These hydrocarbons were cyclohexene, p-xylene and n-hexane. Cyclohexene reacts already on weak acid centres, while p-xylene is transformed on strong acid centres and n-hexane on superacid centres. The product of cyclohexene reaction is chiefly methylcyclopentene; p-xylene gives o- and m-xylene and to lesser extent also benzene and toluene. The reaction of n-hexane

leads to hexane isomers. The catalytic activity of the samples was measured using a glass tube reactor (6 mm internal diameter) in pulse arrangement. The weighed amount of the catalyst was 0·4 g, nitrogen flow rate 20 ml/min, the injected pulses had volume of 1 μl. The reaction temperature was 125°C for cyclohexene, 250°C for p-xylene and 150°C for n-hexane.

RESULTS AND DISCUSSION

Aluminium Oxide (Alumina)

The use of sulphuric acid and ammonium fluoride made it possible to bond considerable amount of modifying groups on alumina while treatment with ammonium chloride introduced only small amount of chlorine on alumina. The amount of phosphate ions deposited on alumina could not be determined with accuracy (Table I). The number of modifying groups bonded to alumina surface decreased with increasing temperature of calcination.

From sorption data it becomes evident that none of the modification agents increased significantly the number of acid centres. The modification of alumina by sulphuric and phosphoric acid has decreased the number of acid centres by c. 50 per cent, compared to the unmodified alumina.

The ratio of the number of all acid centres (pyridine sorption) to the strong ones (benzene sorption) was c. 2 : 1 for the samples modified with H_2SO_4, NH_4Cl and NH_4F and c. 3·5 : 1 for the samples modified with H_3PO_4.

As follows from Table I, strong acid centres exist on the sulphated alumina calcined at 650 and 800°C and on the fluorinated alumina calcined at 800°C. The other samples contained only medium or weak acid centres. Comparison of the amount of modifying groups with the maximum strength of the acid centres of modified aluminas has shown that the acid strength of these centres is not directly proportional to the amount of modifying groups.

It was found that IR spectra of the pyridine bonded on the samples of the unmodified alumina as well as on the catalysts Al_2O_3/H_3PO_4, Al_2O_3/NH_4Cl (after calcination at 650 and 800°C) and Al_2O_3/H_2SO_4 (after calcination at 500°C) did not show the 1 540 cm^{-1} band (Fig. 1b). On the basis of literature data[21−23] it can be accepted that these catalysts contain only the coordinatively bonded pyridine. On the other hand, in addition to the absorption bands corresponding to the coordinatively bonded pyridine, the IR spectra of the other catalysts exhibited also the absorption band at 1 540 cm^{-1} which can be ascribed to the pyridine bonded ionically to protic acid centres.

The absorption bands with maxima at 1 447 and 1 598 cm^{-1} can be assigned to pyridine bonded to surface hydroxy groups via hydrogen bonding or to pyridine bonded to weak protic centres. With respect to the high calcination temperature used and to a small probability of rehydration of the samples, it seems likely that these absorption bands correspond rather to pyridine bonded to aprotic acid centres.

In the case of sulphated alumina, the spectra of the samples prepared at 650 and 800°C differ markedly from the spectrum of the samples prepared at 500°C (Figs 1c and 1d), which does not show any band near 1 540 cm^{-1}, i.e. the band belonging to the pyridine bonded to protic acid centres. This band, however, has been observed in the spectrum of the samples prepared at higher temperatures. Therefore, one can conclude that the samples of the sulphated alumina calcined at 650 and 800°C contain protic acid centres, in contrast to the sample prepared at 500°C. This result is of interest since it can be expected that the higher temperature would lead generally to the decrease in the number of protic centres, as reported e.g. by Ghost[11] for fluorinated alumina.

By catalytic activity measurements it has been found that all the catalysts prepared showed the same or higher catalytic activity toward cyclohexene as the unmodified alumina, although the number of acid centres did not change much by modification. One can thus conclude that all the modification agents are capable of increasing the strength of acid centres.

The catalytic activity for the reactions of *p*-xylene which require the stronger acid centres was exhibited only by the samples of alumina modified with NH_4F and H_2SO_4. The catalytic activity for n-hexane isomerization which demands even stronger acid centres was detected only for Al_2O_3/H_2SO_4 samples calcined at 650 and 800°C. The catalytic activity of the fluorinated alumina toward all the reactants
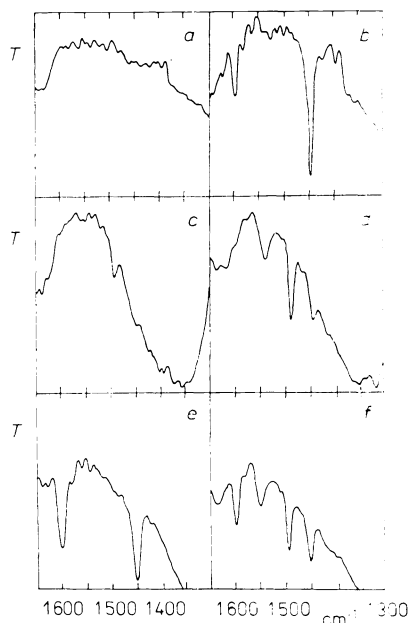

FIG. 1

IR spectra of pyridine sorbed on alumina and silica samples: *a* alumina calcined at 800°C, without pyridine (background); *b* alumina calcined at 650°C; *c* alumina modified with H_2SO_4 and calcined at 500°C; *d* alumina modified with H_2SO_4 and calcined at 650°C; *e* silica calcined at 500°C; *f* silica modified with H_2SO_4 and calcined at 500°C

increased proportionally to the calcination temperature, despite of the fact that the number of acid centres decreased with increasing temperature.

TABLE I

Properties of samples of modified alumina (weak absorption bands in parentheses)

Modification agent (ion)	Unmodified			$H_2SO_4(SO_4^{2-})$		
Preparation temp., °C	500	650	800	500	650	800
Element content, mmol/g	—	—	—	4·4	2·4	1·2
Pyridine sorption, mmol/g	0·61	0·53	0·30	0·31	0·50	0·42
Benzene sorption, mmol/g	0·25	0·25	0·22	0·08	0·29	0·27
Maximum strength of acid centres $(-H_0)$	5·6	5·6	5·6	5·6	13·2	8·2
Absorption maxima, cm^{-1}	1 446	1 446	1 446		1 446	
				1 494	1 491	1 490
					1 541	1 542
	1 594	1 594	1 595			
Cyclohexene conversion, %	0	0	0	79·4	99·8	90·5
p-Xylene conversion, %	0	0	0	5·5	88·9	34·5
n-Hexane conversion, %	—	—	—	0	0·8	0·2

[a] Phosphorus content could not be determined.

TABLE II

Properties of samples of modified silica (weak absorption bands are in parentheses)

Modification agent (ion)	Unmodified			$H_2SO_4(SO_4^{2-})$		
Preparation temp., °C	500	650	800	500	650	800
Element content, mmol/g	—	—	—	0·11	0·09	0·07
Pyridine sorption, mmol/g	1·87	1·09	0·82	1·63	1·41	1·24
Benzene sorption, mmol/g	0·03	0	0	0·34	0·04	0
Absorption maxima, cm^{-1}	1 488	(1 488)	(1 488)	1 447	1 447	1 447
	(1 491)			1 490		
	(1 578)			1 548		
	1 598			1 598	1 598	1 597
Cyclohexene conversion, %	0	0	0	?[a]	?[a]	2·75

[a] Reaction products deposited on the catalyst.

In the case of the samples modified with H_2SO_4, NH_4Cl and H_3PO_4, the highest catalytic activity for cyclohexene conversion was observed for the samples calcined

TABLE I

(*Continued*)

$H_3PO_4(PO_4^{3-})$			$NH_4Cl(Cl^-)$			$NH_4F(F^-)$		
500	650	800	500	650	800	500	650	800
a	*a*	*a*	0·76	0·56	0·54	4·1	3·1	1·8
0·29	0·27	0·21	0·73	0·68	0·53	0·53	0·44	0·24
0·11	0·08	0·05	0·40	0·30	0·28	0·18	0·14	0·12
3·0	3·0	3·0	5·6	5·6	3·0	3·0	5·6	8·2
1 450		(1 450)	(1 447)	1 446	1 446	1 447	1 447	1 447
1 493		(1 490)	1 490			1 493	1 493	1 493
		(1 541)	1 542			1 542	1 547	1 544
						(1579)	(1 579)	(1 598)
			1 590	(1 595)		(1 598)	(1 598)	1 598
6·1	21·7	2·2	4·1	37·0	2·2	21·9	48·1	97·6
0	0	0	0	0	0	0·8	8·5	71·3
—	—	—	—	—	—	—	—	0

TABLE II

(*Continued*)

$H_3PO_4(PO_4^{3-})$			$NH_4Cl(Cl^-)$			$NH_4F(F^-)$		
500	650	800	500	650	800	500	650	800
0·11	0·07	0·05	0·76	0·56	0·54	4·1	3·1	1·8
1·53	0·62	0·21	0·73	0·68	0·53	0·53	0·44	0·24
0·03	0	0·05	0·40	0·30	0·28	0·18	0·14	0·12
1 447	1 447	(1 450)	(1 447)	1 446	1 446	1 447	1 447	1 447
(1 490)	(1 490)	(1 490)	1 490			1 493	1 493	1 493
		(1 541)	1 543			1 542	1 547	1 544
1 598	1 598					(1 579)	(1 579)	(1 578)
				1 590	(1 595)	(1 598)	(1 598)	(1 598)
0	0	0	27·5	0·6	0·03	0·5	1·7	0·5

at 650°C. Sample of the sulphated alumina calcined at 650°C showed also the highest activity in *p*-xylene reaction.

Comparison of IR results with catalytic tests shows that a more significant catalytic activity is exhibited only by the samples which contain protic acid centres. This finding comports with the assumption of Oelderick[25] and Franck[26] about aprotic centres as catalytically inactive in skeletal isomerization of hydrocarbons. This conclusion can be further supported by the results of the measurements of properties of the samples of sulphated alumina. Here, the sample prepared at 500°C, as the only one of the sulphated alumina, does not contain protic acid centres. Accordingly, this sample also shows lower catalytic activity compared with the sample prepared at 650 and 800°C.

The strength, number and catalytic activity of acid centres of the samples of sulphated alumina depended strongly on calcination temperature. The catalyst prepared at 500°C contained only weak acid centres, the catalysts calcined at 650 and 800°C possessed acid centres of the superacid type. The dependence of the strength of acid centres on calcination temperature of similar kind was reported[16,29] for sulphated ZrO_2 and SnO_2. Phosphatation of alumina results in only weakly acidic and low active catalyst. This indicated that we have not been successfull in reproducing the results achieved by Krzywicki[27] for the alumina modified with 0.2 mmol/g H_3PO_4 who found acid centres of the strength $H_0 < -12.7$. The formation of the not too strong acid centres on the surface of alumina modified with NH_4Cl $(H_0 \approx -5.6)$ agrees well with reported data. It is known that the strong acid centres on the surface of alumina are formed where surface chlorine concentration amounts to c. 7 up to 16 per cent[20], whereas the chlorine content of the samples prepared by us was c. 2 per cent. Fluorination of alumina made it possible to prepare a strongly acidic catalyst. These results comport with reported data[28].

Silicon Dioxide (Silica)

It follows from Table II that in contrast to alumina, smaller amounts of foreign ions can be bonded to silica in most cases. The modification of silica with H_2SO_4, H_3PO_4 and NH_4Cl almost did not affect the pyridine or benzene sorption. Modification of silica by NH_4F led to the decrease of the number of acid centres by 10% in comparison with the unmodified silica. The lower amount of pyridine sorbed on fluorinated silicas can be explained by the preferential reaction of NH_4F with the more active OH groups capable of pyridine sorption which decreases the number of acid centres.

In most of the samples of modified silica, pyridine sorption was higher than for the modified alumina (Table I). On the other hand, benzene sorption on the modified silica was substantially lower than that on the modified alumina. This indicates that the modified silica has substantially smaller number of strong acid centres, compared with the modified alumina.

By measuring the maximum strength of acid centres, we have found that the samples of both modified and unmodified silicas contain only weak acid centres of $H_0 = -3$. The exception are the samples of sulphated silica prepared at 500 and 650°C which contain acid centres of medium strength $(H_0 = -5\cdot6)$.

The IR absorption maxima for the samples of modified SiO_2 are given in Table II. Except for the SiO_2/H_2SO_4 sample prepared at 500°C, none of the other samples of modified and unmodified silicas showed the absorption band at $1\,540\,cm^{-1}$, demonstrating that these catalysts do not contain protic acid centres (Figs 1e, 1f).

IR spectra of the unmodified SiO_2 and of the catalysts SiO_2/NH_4Cl, SiO_2/H_3PO_4 and SiO_2/H_2SO_4 (after calcination at 650 and 800°C) show relatively strong absorption bands which could be ascribed to pyridine bonded via weak coordination bond $(1\,447,\,1\,490$ and $1\,595\,cm^{-1})$. The SiO_2/H_2SO_4 samples prepared at 500°C show also an absorption band at $1\,549\,cm^{-1}$ that can be assigned to the pyridine bonded to protic acid centres. The spectra of the fluorinated silica did not exhibit any strong absorption band and did not differ practically from the spectrum of the unmodified silica without pyridine. This result can be related to the very small amount of pyridine sorbed on these samples.

From Table II it can be further concluded that the catalytic activity of the most samples of modified silica for the reactions of cyclohexene is low. The samples of the sulphated silica calcined at 500 and 650°C induced polymerisation of cyclohexene, to form dark reaction products which deposited on the catalysts and were not detectable by chromatography. No catalyst was active for p-xylene and n-hexane reactions.

None of the modification agents enabled us to prepare strongly acidic catalyst. The highest strength of acid centres $(H_0 = -5\cdot6)$ was achieved in the case of the sulphated silica. The low acidity corresponded to the low catalytic activity. Our results comport with reported data[30,31] on the presence of only weak acid centres on sulphated and phosphated silicas.

Tin Dioxide

None of the prepared catalysts showed measurable pyridine or benzene sorption. Exception was only the SnO_2/H_2SO_4 sample calcined at 500°C on which pyridine sorbed amounted to c. $0\cdot01\,mmol/g$. The catalytic activity for cyclohexene isomerization of all the samples was negligible (max. $0\cdot05\%$). The activity toward p-xylene and n-hexane was not detectable.

The SnO_2/H_2SO_4 sample after calcination at 500°C possessed acid centres of the strength $H_0 = -3$, the other samples did not contain the centres of $H_0 \leqq -3$.

It has been found that the tin dioxide used is not suitable as the starting material for the synthesis of acid centres by impregnation procedure. This fact can be related to the low content of the modification agents introduced into the catalysts.

It is known in the literature that the sulphated SnO_2 can possess increased acidity compared with the unmodified SnO_2. However, Arata[16] suceeded in preparing the catalyst with superacid centres ($H_0 = -16.04$). The samples prepared by Wang[32] and by Jin[15] contained acid centres of medium strength. However, the authors started from $Sn(OH)_4$ and not from SnO_2 as we did in the present work. One can conclude that inert tin dioxide is not suitable starting material for preparation of acid catalysts based on chemically modified SnO_2 by impregnation. Under the conditions used, modification agents do not react with the dioxide surface.

Titanium Dioxide

From Table III it is evident that except for H_2SO_4, no impregnation agent was able to introduce higher amounts of modifying ions on TiO_2 surface. No catalyst sorbed measurable amounts of pyridine or benzene. Only the TiO_2/H_2SO_4 sample calcined at $500°C$ contained very small amount of both bases (estimated to be c. 0.005 mmol/g). The TiO_2/H_2SO_4 samples calcined at 500 and $650°C$ showed medium acid centres of $H_0 = -5.6$, whereas the other samples contained only weak acid centres of $H_0 = -3$.

TiO_2 samples modified with NH_4F, NH_4Cl, and H_3PO_4 did not exhibit any activity for cyclohexene reaction. The catalysts prepared by sulphatation of TiO_2 showed relatively high initial activity for the reactions of cyclohexene. Thus, with the sample calcined at $500°C$, cyclohexene conversion was c. 64%, with that calcined at $650°C$ cyclohexene reacted with 22% conversion and with the sample calcined at $800°C$, the cyclohexene conversion was found to be c. 0.5 per cent. The activity of these catalysts decreased rapidly in the course of the reaction.

There exist several works which are concerned with the sulphatation of TiO_2. Hino[13,14] prepared the catalyst with centres of $H_0 = -13.76$, the other authors[33,34] obtained only the catalysts with acid centres of medium strength. Unfortunately,

TABLE III
Content of modifying ions in TiO_2

Modification agent Modifying ion	H_2SO_4 SO_4^{2-}	H_3PO_4 PO_4^{3-}	NH_4Cl Cl^-	NH_4F F^-
Ion content (mmol/g)				
After calcination				
at 500°C	0.82	0.04	0.54	0.30
at 650°C	0.39	0.02	0.23	0.14
at 800°C	0.07	0.01	0.08	0.10

our attempt at reproducing these results has failed. This fact can be explained, similarly as in the case of SnO_2, by the use of TiO_2 as the precursor in place of titanium(IV) hydroxide which was used in the above mentioned studies.

Zirconium Dioxide

Two forms of zirconium dioxide (black and white modifications) were subjected to study. Because of the insufficient amount of the oxide available in our laboratory, we decided to modify the oxide only by sulphuric acid and by ammonium fluoride. The properties of the samples of modified ZrO_2 are presented in Table IV. The pure ZrO_2 was catalytically inactive and also the amount of pyridine or benzene sorbed on its surface was not measurable.

The strength of acid centres of the most samples could not be measured because of the discolouration of the samples. The samples of the sulphated white modification of zirconium dioxide were proved to contain acid centres of the strength $H_0 < -8$. The catalytic activity of the samples of sulphated zirconium dioxide was rather high, although the samples contained only relatively small amount of acid centres. Such a low content of acid centres can be explained by the small specific surface of the starting dioxide which was c. $0.2 \text{ m}^2/\text{g}$ for the black modification and c. $4.5 \text{ m}^2/\text{g}$ for the white modification. As a consequence of the small amount of acid centres, we have not been able to prove reliably whether the samples contain on their surface acid centres active for n-hexane isomerization. The effect of fluorination of ZrO_2 on its acidity was small.

TABLE IV

Properties of samples of modified ZrO_2

Modification agent (Modifying ion)	ZrO_2 modification	Calcination temp., °C	Pyridine sorption mmol/g	Cyclohexene conversion	p-Xylene conversion
H_2SO_4 (SO_4^{2-})	black	500	0	30·0	0·3
		650	0	14·7	traces
	white	500	>0	~94	~12
		650	0·08	~85	~7
NH_4F (F^-)	black	500	0	0·4	0
		650	0	0·2	0
	white	500	0	3·3	0
		650	0	2·8	0

Zirconium Silicate

As found by elemental analysis, the sample modified with NH_4Cl and H_3PO_4 did not contain chlorine or phosphorus. The contents of fluorine and sulphur in the samples modified with H_2SO_4 and NH_4F are given in Table V.

None of the prepared samples of modified $ZrSiO_4$ showed measurable pyridine or benzene sorption. The maximum strength of the acid centres could be estimated only for the sulphated samples. The other samples were dark, which interferred with the colour of the indicator. The $ZrSiO_4/H_2SO_4$ samples calcined at 500 and 650°C contained acid centres of $H_0 = -8.2$ and the $ZrSiO_4/H_2SO_4$ sample calcined at 800°C possessed acid centres of $H_0 = -3$.

Neither the unmodified zirconium silicate nor the zirconium silicate modified with H_3PO_4 showed any catalytic activity. Some catalytic activity (cyclohexene conversion c. 0.2%) was found for the samples of $ZrSiO_4$ modified with NH_4Cl and NH_4F and calcined at 500°C. The substantially higher activity toward cyclohexene was determined for the sulphated samples. Thus, the sample calcined at 500°C was found to cause 15.1% cyclohexene conversion, the sample calcined at 650°C 3.7% and that calcined at 800°C only 0.2% conversion. Any of the samples did not show measurable activity toward p-xylene; only with the $ZrSiO_4/H_2SO_4$ calcined at 500°C, traces of the product were detected as the result of the reaction.

The effect of phosphoric acid, ammonium chloride and ammonium fluoride on the acidity of zirconium silicate was negligible. The reason is very likely the fact that these substances are not able to interact with the rather inert silicate during its impregnation. It can be assumed that the sulphatation of zirconium silicate forms only small number of strong acid centres and that this process could lead to the catalysts of similar properties to those obtained by sulphatation of zirconium dioxide.

TABLE V

Content of modifying ions in samples of $ZrSiO_4$

$T_{calc.}$ °C	SO_4^{2-} mmol/g	F^- mmol/g
500	0.03	0.05
650	0.02	0.02
800	0.01	0

Antimony Trioxide

Calcination of Sb_2O_3 was carried out at 500 and 650°C only (the oxide melts at 656°C). We suceeded in introducing only relatively small amount of modifying ions on the oxide $(0.01-0.02 \text{ mmol/g})$. Somewhat higher content of chlorine was found for the sample modified with ammonium chloride $(0.11-0.36 \text{ mmol/g})$. None of the prepared catalysts showed measurable pyridine or benzene sorption. The catalytic activity of the samples was negligible. None of the samples contained acid centres of the strength $H_0 = -3$.

Evaluation of the Impregnation Procedures for Synthesis of Acid Catalysts

The modification agents can be arranged according to their effect on the acidity of the oxides to the following series:

$$H_2SO_4 \gg NH_4F > NH_4Cl, H_3PO_4 .$$
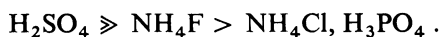
One can state that the increase of the strength and number of acid centres of the oxides is not usually proportional to the content of modifying ions. With regard to the effect of chemical modification on their acidity, the oxides can be divided into three groups. The first group includes alumina and zirconium silicate. Some of the catalysts prepared from these oxides show catalytic activity for *p*-xylene conversion. In the case of alumina, the use of sulphuric acid has resulted in the catalyst containing superacid centres $(H_0 = -13.2)$ and the use of ammonium fluoride led to the catalyst with strong acid centres $(H_0 = -8.2)$. The sulphatation of zirconium silicate afforded the catalyst containing acid centres of the strength $H_0 = -8.2$.

The second group includes SiO_2, SnO_2 and TiO_2. Modification of these oxides led to the catalysts with medium acid centres $(H_0 \approx -5.6)$. These catalysts were active for reactions of cyclohexene, being inactive however for *p*-xylene conversion. Comparison of their catalytic activity with the number of acid centres shows that the acid centres of the modified silica are substantially less active than the acid centres of the modified titanium and tin dioxides.

The third group includes antimony trioxide, the surface acidity of which could not be increased by any of the modification agents used in the present study.

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