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

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Acid properties of the oxides Al_2O_3, SiO_2, TiO_2, SnO_2, Sb_2O_3, ZrO_2 and $ZrSiO_4$ were modified by the action of Lewis acids. The acids ($AlCl_3$, $TiCl_4$, PCl_5, SbF_5 and P_2O_5) were deposited on the oxides by sublimation at 150, 250 and 350°C. The strength and number of acid centres of the prepared catalysts and their catalytic activity in hydrocarbon reactions were determined.

The surface acidity of some oxides can be markedly affected by their chemical modification by Lewis acids[1−4]. The aim of this work was the synthesis of acid catalysts by deposition of the Lewis acids ($AlCl_3$, $TiCl_4$, PCl_5, SbF_5 and P_2O_5) on the oxides (Al_2O_3, SiO_2, TiO_2, SnO_2, Sb_2O_3, ZrO_2 and $ZrSiO_4$) and characterization of their acidic and catalytic properties. The present work continues our previous study[5] on the impregnation procedure for the synthesis of strongly acidic catalysts by modification of the same oxides.

EXPERIMENTAL

Compounds used. The same oxides as in our previous work[5] were used for the synthesis of acid catalysts. The surface area of the oxides calcined at 150, 250 and 350°C was almost identical to the surface after calcination at 105°C (ref.[5]). Antimony pentafluoride (Merck, per analysis), aluminium chloride (Fluka, pure, Fe < 0·008%), phosphorus pentachloride (Reachim, pure), titanium tetrachloride (Fluka, technical purity grade), phosphorus pentoxide (Lachema, per analysis), dimethyl zinc (prepared according to the reported procedure[6]).

Catalyst preparation. The oxide dried at 150, 250 and 350°C, respectively (nitrogen flow rate 30 ml/min) was treated for 30 min with the modification agent ($AlCl_3$, $TiCl_4$, PCl_5, SbF_5 or P_2O_5) in a stream of nitrogen at the same temperature at which the oxide was dried. The excess modification agent (i.e. the agent which did not react with the oxide surface) was removed by heating the sample in nitrogen (flow rate 60 ml/min) at 350°C for 80 min. The properties of prepared samples were characterized similarly as in our previous work[5]. The content of surface OH groups in the starting oxide was determined by titration with dimethyl zinc[6].

RESULTS AND DISCUSSION

Aluminium Oxide (Alumina)

The starting alumina after calcination at 150, 250 and 350°C contained 4·18, 3·62 and 2·56 mmol/g OH groups, respectively. The content of the modifying elements on alumina surface due to the use of the modification agents is given in Table I.

The chemical modification of alumina resulted in most cases in an increase of both the total number of acid centres (pyridine sorption) and the number of strong acid centres (benzene sorption). The maximum strength of acid centres depended markedly on the used modification agent. As found, the sample modified with aluminium chloride, titanium tetrachloride, and phosphorus pentachloride showed superacid centres; the modification of alumina with antimony trifluoride or phosphorus pentoxide afforded only medium or weak acid centres.

The IR absorption maxima of pyridine bonded on the samples of modified alumina are given in Table I. The spectra of the unmodified alumina and alumina samples modified with phosphorus pentoxide show only absorption bands corresponding to the coordinatively bonded pyridine[7,8], i.e. the bands at 1 450, 1 595 and 1 615 cm^{-1} (Fig. 1b). Furthermore, the spectra of the other catalysts show also a band at 1 540 cm^{-1} which can be assigned to the pyridine bonded to protic centres (Figs 1c, 1d).
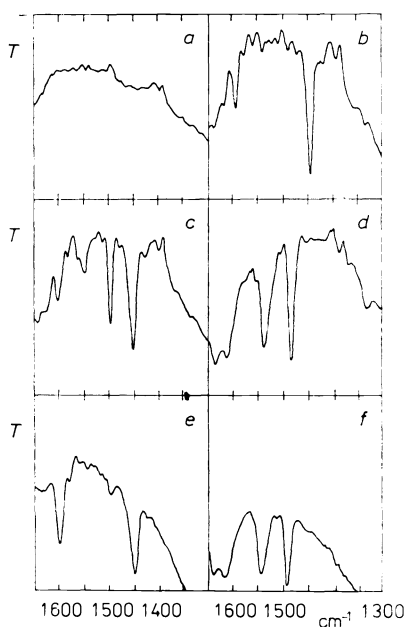

FIG. 1
IR spectra of pyridine sorbed on alumina and silica samples: *a* alumina calcined at 150°C, without pyridine (background); *b* alumina calcined at 250°C; *c* alumina modified with SbF$_5$ and calcined at 250°C; *d* alumina modified with PCl$_5$ and calcined at 250°C; *e* silica calcined at 250°C; *f* silica modified with TiCl$_4$ and calcined at 250°C

The absorption bands at 1 450, 1 595 and 1 615 cm^{-1} can be ascribed to the pyridine bonded via hydrogen bonding to surface hydroxy groups and the pyridine bonded to aprotic centres of lower acidity[8].

The spectra of the samples $Al_2O_3/AlCl^3$ and Al_2O_3/PCl_5 were very similar and their pattern was not dependent on the condition used for sample preparation. The absorption spectra of these aluminas are of interest as in contrast to the other samples, they do not contain the 1 447 cm^{-1} band, i.e. one of the bands related to the coordinatively bonded pyridine.

All the modified aluminas showed higher catalytic activity for hydrocarbon conversions than did the unmodified alumina. The high catalytic activity was found especially with aluminas modified by chlorinating agents. The catalytic activity of these catalysts was not directly proportional to the chlorine content. This indicates that different chlorinating agents form different kinds of acid centres on alumina.

Comparison of the spectroscopic with activity data in Table I shows that similarly to the samples of alumina prepared by impregnation procedure, the enhanced catalytic activity is exhibited only by the samples which contain acid centres of protic type.

Silicon Dioxide (Silica)

The silica used for synthesis of the catalysts contained after calcination at 150, 250 and 350°C 1·18, 0.85 and 0·82 mmol/g exchangable hydrogens, respectively. The amount of modifying elements which could be deposited on silica surface is given in Table II.

Although we were able to introduce on silica relatively great amount of modifying elements, none of the agents used affected significantly the sorption of pyridine, i.e. the total number of acid centres of silica (Table II). The modification of silica with $AlCl_3$, $TiCl_4$ and P_2O_5, respectively, has resulted, however, in the substantial increase of the number of strong acid centres (benzene sorption) when compared with the unmodified silica. As found by the indicator method, no sample of the modified silica contained weak or medium acid centres in greater amounts.

IR spectra of individual samples of the modified silica were of similar type. All the spectra showed strong absorption bands corresponding to pyridine bonded to aprotic acid centres or to surface OH groups (the bands at around 1 620, 1 491 and 1 448 cm^{-1}) and weak absorption bands corresponding to pyridine bonded to protic acid centres $(1\ 540\ cm^{-1})$ (cf. Figs 1d, 1e). On the other hand, only the bands corresponding to the coordinatively bonded pyridine were found for the unmodified silica.

The catalytic activity for cyclohexene conversion was found to be comparable for all the samples of modified silica. None of the catalysts showed measurable activity for the reaction of p-xylene (traces of the product were found for the samples

$SiO_2/AlCl_3$ and $SiO_2/TiCl_4$). In testing the samples SiO_2/SbF_5 for p-xylene conversion, a dark zone has been found in the catalyst layer. However, the reaction did not

TABLE I

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

Modification agent (element)	Unmodified			$AlCl_3(Cl)$		
Preparation temp., °C	150	250	350	150	250	350
Element content, mmol/g	—	—	—	2·13	2·07	2·03
Pyridine sorption, mmol/g	0·26	0·37	0·51	1·32	1·06	1·16
Benzene sorption, mmol/g	0·06	0·14	0·24	0·32	0·28	0·22
Maximum strength of acid centres $(-H_0)$	3·0	3·0	3·0	13·2	14·5	13·2
Absorption maxima, cm^{-1}	1 445	1 445	1 446			
				1 488	1 488	1 488
				1 540	1 540	1 540
	(1 594)	1 595	(1 594)			
	(1 618)			(1 614)	(1 613)	(1 614)
Cyclohexene conversion, %	∼0	∼0	0·1	93·7	92·9	97·8
p-Xylene conversion, %	0	0	0	30·9	85·1	87·2
n-Hexane conversion, %	0	0	0	1·0	3·8	6·1

TABLE II

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

Modification agent (element)	Unmodified			$AlCl_3(Cl)$		
Preparation temp., °C	150	250	350	150	250	350
Element content, mmol/g	—	—	—	0·20	0·33	0·52
Pyridine sorption, mmol/g	1·89	1·98	1·65	1·99	2·35	1·06
Benzene sorption, mmol/g	0·03	0·02	0·04	0·45	0·45	0·31
Maximum strength of acid centres $(-H_0)$	a	a	a	3·0	3·0	5·6
Absorption maxima, cm^{-1}	1 448	1 447	1 448	1 447	1 448	1 448
	(1 490)	(1 494)	(1 491)	1 490	1 491	1 490
				(1 542)	(1 543)	(1 543)
	1 599	1 599	1 599	1 599	1 598	1 598
Cyclohexene conversion, %	0	0	0	3·0	4·6	∼17

^{a} Catalysts did not contain acid centres of the strength $H_0 < -3$.

afford any product which could be detected by FID detector. It seems likely that condensation reactions were taking place, giving polyaromatic compounds. None

TABLE I

(*Continued*)

TiCl$_4$(Cl)			PCl$_5$(Cl)			SbF$_5$(F)			P$_2$O$_5$(F)		
150	250	350	150	250	350	150	250	350	150	250	350
0·70	0·73	1·34	2·05	1·85	7·53	7·53	5·57	6·64	—	—	—
0·76	0·84	1·05	1·18	1·11	1·11	0·31	0·34	0·37	0·33	0·39	0·57
0·28	0·24	0·30	0·24	0·21	0·20	0·13	0·21	0·04	0·21	0·20	0·20
13·2	13·2	14·52	14·52	14·52	13·2	5·6	5·6	5·6	3·0	3·0	3·0
1 447	(1 448)	(1 338)				1 447	1 447	1 447	1 448	1 446	1 447
1 490	1 488	1 489	1 489	1 489	1 489	1 493	1 493	1 493	(1 493)	(1 493)	(1 493)
1 541	1 540	1 541	1 541	1 541	1 542	(1 542)	(1 542)	1 542			
						(1 498)	(1 498)	(1 498)	(1 594)	(1 594)	(1 594)
(1 616)	(1 614)	(1 615)	(1 615)	(1 615)	(1 615)				(1 617)		(1 618)
93·1	92·9	92·1	81·7	83·0	94·0	31·3	40·8	27·0	0·4	3·2	17·4
50·2	43·2	32·5	48·3	37·3	20·5	2·1	3·0	1·4	0	0	0
0·4	0·1	~0	5·2	2·1	~0	0	0	0	0	0	0

TABLE II

(*Continued*)

TiCl$_4$(Cl)			PCl$_5$(Cl)			SbF$_5$(F)			P$_2$O$_5$(P)		
150	250	350	150	250	350	150	250	350	150	250	350
0·62	1·78	1·85	1·79	3·05	2·55	3·40	3·14	2·84	2·87	2·06	1·44
1·79	1·99	1·16	0·75	1·08	1·15	1·13	1·63	1·12	1·01	2·06	1·44
0·36	0·37	0·34	0·12	0·08	0·02	0·08	0·10	0·02	0·48	0·53	0·28
3·0	3·0	3·0	5·6	3·0	3·0	5·6	5·6	3·0	*a*	*a*	3·0
1 447	1 447	1 447			(1 457)	(1 448)	(1 448)	(1 448)	(1 447)		(1 449)
1 490	1 484	1 484	1 490	1 490	1 490	1 491	1 491	1 491	(1 492)	1 492	(1 495)
(1 543)	(1 541)	(1 541)	(1 541)	(1 540)	(1 543)	(1 543)	(1 543)	(1 543)		(1 547)	(1 541)
(1 598)	(1 598)	(1 598)							(1 592)		1 599
(1 616)	(1 615)	(1 616)	1 616	1 616	1 618	(1 616)	(1 619)	(1 619)			
9·4	10·9	10·6	22·6	7·6	7·0	9·3	10·8	8·1	5·0	13·2	8·2

of the prepared samples exhibited catalytic activity for reactions of n-hexane, by contrast to Melchor[4] who prepared a superacid catalyst by deposition of aluminium chloride on silica.

Titanium Dioxide

The titanium dioxide samples contained after calcination at 150, 250 and 350°C 0·27, 0·25 and 0·23 mmol/g of exchangable hydrogens, respectively.

In contrast to silica and alumina, only small amount of modifying elements could be introduced on titanium dioxide surface (Table III). It seems likely that TiO_2 cannot be modified with PCl_5 and $TiCl_4$. In most cases, a significant number of acid centres is not formed here by the modification of titanium dioxide. Benzene sorption was measurable only with the samples modified by $AlCl_3$ and P_2O_5, the amount of sorbed benzene being however low (max. 0·2 mmol/g).

TABLE III

Properties of modified TiO_2

Modification agent (element)	Unmodified			$AlCl_3(Cl)$		
Preparation temp., °C	150	250	350	150	250	350
Element content, mmol/g	—	—	—	0·12	0·33	0·59
Pyridine sorption, mmol/kg	0	0	0	[a]	0·30	0·26
Cyclohexene conversion, %	0	0	0	0·2	~5[b]	~10[b]

[a] The amount of pyridine sorbed was less than 0·01 mmol/g. [b] The activity of the catalyst de

TABLE IV

Properties of samples of modified SnO_2

Modification agent (element)	Unmodified			$AlCl_3(Cl)$		
Preparation temp., °C	150	250	350	150	250	350
Element content, mmol/g	—	—	—	0·08	0·05	0·03
Cyclohexene conversion, %	0	0	0	0·2	0·1	0·1

[a] The activity of the catalyst decreased fast during the reaction.

None of the prepared catalysts was found to contain acid centres of the strength $H_0 < -5.6$. A more distinct catalytic activity toward cyclohexene was observed only with samples of titanium dioxide modified with $AlCl_3$ and P_2O_5. No sample was active for p-xylene and n-hexane conversions.

Tin Dioxide

The tin dioxide contained after calcination at 150, 250 and 350°C 0.20, 0.18 and 0.17 mmol/g of exchangable hydrogens, respectively. The content of modifying elements in the samples was low (Table IV).

Pyridine sorption varied from 0.15 to 0.97 mmol/g for the SnO_2/P_2O_5 samples, being less than 0.10 mmol/g for the other samples. Benzene sorption was very low or immeasurable (max. 0.05 mmol/g). The samples modified with P_2O_5 possessed acid centres of the strength $H_0 < -5.6$, the other samples contained acid centres of the strength $H_0 < -3$.

TABLE III
(Continued)

TiCl₄(Cl)			PCl₅(Cl)			SbF₅(F)			P₂O₅(P)		
150	250	350	150	250	350	150	250	350	150	250	350
0.02	0.13	0.24	0.04	0.17	0.18	1.32	1.02	1.29	2.44	2.00	1.05
a	*a*	*a*	*a*	*a*	*a*	0.06	0.03	0.04	0.85	1.23	0.20
0.1	0.4	0.6	0.1	0.3	0.9	13.5	2.6	2.6	37.6	29.7	8.9

creased fast during the reaction.

TABLE IV
(Continued)

TiCl₄(Cl)			PCl₅(Cl)			SbF₅(F)			P₂O₅(F)		
150	250	350	150	250	350	150	250	350	150	250	350
0.04	0.04	0.03	0.03	0.03	0.03	0.22	0.19	0.14	0.55	0.66	0.98
0	0	0	0	0	0	1.4	4.6	0.2	1.8	~37[a]	12.1

The weak strength of acid centres of the samples of modified tin dioxide comports with their low activity for cyclohexene conversion (Table IV). No sample showed catalytic activity for the reactions of p-xylene and n-hexane.

Zirconium Dioxide and Zirconium Silicate

Both starting compounds contained after calcination at 150, 250 and 350°C approximately the same amount of surface OH groups varying from 0·01 to 0·03 mmol/g. The content of phosphorus in the samples modified with P_2O_5 amounted to 0·2 up to 0·4 mmol/g while the content of the other modification agents was negligible (max. 0·09 mmol/g).

The samples of zirconium dioxide and zirconium silicate modified by phosphorus pentoxide sorbed ca 0·8 mmol/g of pyridine, its amount being immeasurable with the other samples. None of the samples showed measurable benzene sorption. The maximum strength of acid centres could not be determined because of the small number of acid centres and discolouration of some samples. The catalytic activity of the prepared samples for the reaction of cyclohexene was low (conversion max. 3·5%), the catalysts being inactive for p-xylene and n-hexane conversions.

Antimony Trioxide

Preparation of the catalysts was made with Sb_2O_3 that after calcination at 150, 250 and 350°C contained 0·11, 0·11 and 0·09 mmol/g of surface OH groups, respectively.

Although the chemical modification introduced considerable amounts of modification agents on the oxide surface $(1·1-2·7 \text{ mmol/g})$, neither the strength nor the number of surface acid centres were affected. On most samples of modified Sb_2O_3, pyridine sorption was very low, max. 0·06 mmol/g; for the Sb_2O_3/P_2O_5 samples it was 0·13 mmol/g. Benzene sorption was not measurable on any sample. The phosphated samples prepared at 150 and 250°C contained acid centres of the strength $H_0 < -5·6$, the other samples showed acid centres of the strength $H_0 < -3$. The catalytic activity of the samples of modified Sb_2O_3 for the reactions of cyclohexene was very low (conversion max. 0·8%). p-Xylene and n-hexane did not react.

Comparison of the Oxides and Modification Agents

None of the prepared oxides showed a direct proportionality between the content of the introduced heteroatoms and the increase of the strength and number of acid centres or catalytic activity. The catalytic activity of the chlorinated oxides was not proportional to the surface chlorine concentration. A significant effect on acid properties of the oxides has the nature of the modification agent. From this fact one can conclude that different chlorinating agents form different active structures on the

oxide surface. In treatment of the oxides with PCl_5, the outlet gas contained in most cases the chloride of the central atom of the oxide, e.g. $AlCl_3$, $TiCl_4$, etc.

For the oxides used, the proportionality between the content of introduced hetero-atoms and the number of surface OH groups has not been observed. It is thus evident that the deposition of Lewis acids on alumina surface proceeds via more complex mechanism and not only via substitution reaction of the surface hydroxy groups.

Based on the weight increase during deposition of the samples and on the content of halogens determined by elemental analysis, the approximate halogen to metal ratio resulting from treatment of alumina, silica and titanium with modification agents can be calculated (Tables V and VI). This ratio was further used to propose mechanism of the action of modification agents. The calculation was based on the assumption that the weight of the starting alumina and silica samples does not

TABLE V

Approximate halogen to metal molar ratio resulting from treatment of alumina with modification agents. (The ratio could not be calculated for the samples modified with PCl_5 because of the insufficient accuracy of the mass balance. For alumina modified with P_2O_5, phosphorus content was not determined with sufficient accuracy)

Preparation temp., °C	Modification agent		
	$AlCl_3$ Cl/Al	$TiCl_4$ Cl/Ti	SbF_5 F/Sb
150	1·74	0·96	13·71
250	2·66	0·85	6·07
350	9·11	2·68	3·22

TABLE VI

Approximate halogen to metal molar ratio resulting from treatment of silica with modification agents

Preparation temp., °C	Modification agent				
	$AlCl_3$ Cl/Al	$TiCl_4$ Cl/Ti	PCl_5 Cl/P	SbF_5 F/Sb	P_2O_5 O/P
150	2·72	1·33	2·18	3·13	2·41
250	3·71	1·24	4·33	2·11	2·30
350	5·15	1·61	4·04	2·20	1·16

change during deposition of the modification agent (i.e. only negligible amount of the modified oxide is evolved as volatile halogenide during modification).

From Tables V and VI it becomes evident that the ratio in which halogen and metal are bonded to alumina from the modification agent depends strongly on the temperature of sample preparation. Based on data in Tables V and VI, two ways of the action of Lewis acids on alumina could be proposed. In the first one, the action of the modification agent leads to deposition of only the halogen, the metal ion being not introduced on alumina surface. The residue of the Lewis acid containing by one or more halogen atoms less is volatilized and removed by carrier gas. The Lewis acid thus acts here as halogenating agent. This action could result in the higher halogen to metal ratio than is that in the starting Lewis acid.

The second way involves fixation of only the metal ion, one or more halogen atoms being removed as volatile compounds by carrier gas. The most probable mechanism of this reaction is substitution of the surface hydroxy groups by the residue of the Lewis acid. This reaction involves formation of hydrogen halogenide and fixation of the residue of the Lewis acid to alumina via oxygen to form the structure of the type Al—O—MeX_n (where Me denotes metal ion from the Lewis acid and X is halogen). By the above way, more than one halogen atom of the Lewis acid can undergo reaction. In such a case, the metal ion is bonded to alumina surface by several oxygen atoms. This substitution mechanism thus results in the lower halogen to metal ratio, compared with that in the starting Lewis acid.

In most samples, both reactions of Lewis acids with alumina surface were taking place. The resulting metal to halogen ratio was thus dependent on which of the two reactions prevailed in a given case.

Comparison of the effect of the individual modification agents on the strength and number of acid centres of the oxides under study does not lead to unambiguous conclusions. The reason is that the action of some reagents causes an increase of the number of acid centres while other agents affect more the acid strength of these centres.

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Translated by J. Hetflejš.