

ACID-BASE PROPERTIES OF MODIFIED ALUMINAS

E. A. PAUKSHITIS^a, P. I. SOLTANOV^a, E. N. YURCHENKO^a and Květa JIRÁTOVÁ^b^a Institute of Catalysis,

Siberian Division of Academy of Sciences of the U.S.S.R., 630 090 Novosibirsk, USSR and

^b Institute of Chemical Process Fundamentals,

Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát, Czechoslovakia

Received October 12th, 1981

Acid-base properties of the pure alumina and aluminas modified by addition of various ions were determined by IR spectroscopic and Benesi method. The quality and concentration of OH groups of alumina samples containing SO_4^{2-} , F^- , Cl^- , Na^+ , Zn^{2+} and Mg^{2+} ions were determined by IR spectroscopy. Pyridine, benzonitrile and carbon monoxide were used to determine the concentration and strength of aprotic centres and deuteriochloroform was used to determine the concentration and strength of basic centres. The results allowed to evaluate changes in the above properties caused by changes in the concentration of ions in alumina. It was found that the total acidity of modified aluminas determined by Benesi method correlates well with the relative proportion of acidic OH groups in the total spectrum of OH groups.

Active aluminium oxide (alumina) is one of the most frequently used supports for heterogeneous catalysts. Alumina itself is active in a number of catalytic reactions such as dehydration of alcohols, isomerisation of olefins, *etc.* In these reactions the acid-base character of alumina surface plays a role, the relative proportion of acidic and basic centres being dependent on the methods used to synthesize aluminas¹. It seems likely that the different procedure is not the only reason for the differences observed. Certain effect on the surface properties of alumina may be exerted also by impurities by which alumina is contaminated during its preparation, as the result of imperfect removal of ions (*e.g.* Na^+ , SO_4^{2-} , Cl^- , *etc.*) from the precipitate by washing.

The aim of this work was to characterize surface properties of the aluminas modified by various ions by using IR spectroscopy and to ascertain whether there exists a relationship between data obtained by spectroscopy and those obtained by the widely used Benesi titration in nonaqueous medium.

EXPERIMENTAL

Aluminas were prepared by kneading² a commercial aluminium hydroxide of high purity with the appropriate amount of sulphuric, hydrochloric and hydrofluoric acid, sodium hydroxide, magnesium nitrate or zinc acetate, using such an amount of water which ensured formation of the paste extrudable by a piston extruder at a pressure of 4 MPa. The reference alumina sample not containing ions was prepared by kneading aluminium hydroxide with water. The extrudates were dried at 393 K and annealed in a muffle kiln at 873 K for 4 h. The ion content and specific

surface of individual samples are presented in Table I. The specific surface of samples was determined by BET method from the adsorption isotherm of nitrogen at liquid nitrogen temperature.

IR spectroscopy. Acidic properties of aluminas were evaluated from the IR spectra of adsorbed pyridine, benzonitrile, and carbon monoxide. Basic properties of aluminas were determined from the spectra of deuterated chloroform.

Samples in the form of a fine powder were pressed to thin plates, the weight of 1 cm^2 of the tablet ρ being from 12 to 25 mg. The tablets were annealed at 773 K for 2 h in air and for 2 h in vacuum ($P \leq 13 \text{ mPa}$). Carbon monoxide was adsorbed at -110°C and a pressure of 1.3 to 2.0 kPa. Pyridine adsorption was carried out for 15 min at a pressure of *c.* 2 kPa and 423 K, which was followed by desorption at 423 K for 1 h. Benzonitrile was adsorbed at a pressure of 0.83 to 1.3 Pa at 298 K for 15 min. Deuteriochloroform was adsorbed at a pressure of 25–50 kPa at 298 K for 3 min.

The spectra were recorded on UR-20, Zeiss (Jena) spectrometer in the $4000\text{--}1100 \text{ cm}^{-1}$ region at 163–298 K. The spectra were analysed after correction for background by SK-2 curve

TABLE I
Content of ions and specific surface of measured alumina samples

Sample	Ion content		Specific surface m/g^2
	% mass	mmol/g Al_2O_3	
Al_2O_3	0	0	209
SO_4^{2-}	0.5	0.5	198
	1	1.14	226
	2	2.16	242
	3	2.97	233
	5	4.85	239
F^-	0.05	0.05	238
	0.5	0.44	205
	1	1.04	225
	2	2.09	203
	3	2.61	183
	5	4.27	180
Na^+	0.05	0.10	175
	0.5	0.62	208
	1	1.03	200
	3	3.2	165
Zn^{2+}	0.5	0.41	220
	1.5	1.28	203
	2	2.12	210
	5	4.14	206
Mg^{2+}	1	0.89	240
Cl^-	1	0.89	216

synthesizer. The total spectrum was separated into components and the integrated intensity of bands of individual components A_i was determined. The accuracy of band separation was ± 5 per cent. The number of individual bands and their position was determined from the number of observed maxima and shoulders in the total spectrum. To calculate relative concentrations of hydroxyl groups, the A_i values obtained were standardized with respect to the thickness (ρ) of the tablet and to specific surface (S) of sample.

Benesi method. In this case the method of successive approximations was used^{3,4}. The surface acidity was determined by titration with 0.025M solution of n-butylamine in toluene. The following indicators were used: Dimethyl Yellow (pK_a 3.3), benzenazodiphenylamine (1.5), benzalacetophenone (-5.6) and anthraquinone (-8.2). Qualitative evaluation of surface basicity was made with the use of following indicators: Bromothymol Blue (pK_a 7.1), phenolphthalein (9.3), thymolphthalein (9.7), trinitrobenzene (14.4), 2,4-dinitroaniline (15.8), 4-chloro-2-nitroaniline (17.2). Prior to determination, the samples were ground to ≤ 0.08 mm particles and activated by annealing in a furnace at 673 K for 2 h.

RESULTS AND DISCUSSION

Spectra of Starting Alumina

In investigating the surface properties of aluminas we made use of the known facts reported in literature. If the spectrum of adsorbed pyridine exhibits $\nu(\text{CC}(\text{N}))$ band at $1\,540\text{ cm}^{-1}$, this indicates that protic centres are present on the surface of samples⁵. Formation of bands at $1\,455$ and $1\,625\text{ cm}^{-1}$ can be ascribed to aprotic acidic centres. The spectrum of benzonitrile can be used to identify aprotic centres⁵ on the basis of $\nu(\text{CN})$ bands at $2\,250$ – $2\,290\text{ cm}^{-1}$. From the position of $\nu(\text{CO})$ band in the spectrum of carbon monoxide one can determine the strength of aprotic centres⁶ and from the position of $\nu(\text{CD})$ in the spectrum of deuterated chloroform one can judge on the strength of basic centres⁷.

Hydroxyl groups. The IR spectrum of the pure alumina (Fig. 1, curve *a*) exhibits at most seven bands with frequencies $3\,803$, $3\,780$, $3\,756$, $3\,735$, $3\,710$, $3\,690$ and $3\,670\text{ cm}^{-1}$ which are assigned to different types of OH groups. The high frequency OH groups $3\,803$, $3\,780$, $3\,756\text{ cm}^{-1}$ (designated as 1–3 in Table II) form weak hydrogen bonds at 163 K with carbon monoxide. Bands at $3\,803$, $3\,780$ and $3\,756\text{ cm}^{-1}$ shift to the lower frequency region by 30 to 40 cm^{-1} due to hydrogen bonding. In agreement with reported data⁸, the proton affinity (PA) of these OH groups equals to $1\,590 \pm 25\text{ kJ/mol}$ (Table II), which speaks for their weak proton donor properties, so that they can be classified as basic OH groups. In accordance with some proposals^{9,10}, we deal here with the end OH groups bonded to aluminium cation which coordinates oxygen in different ways (from 6 to 4). Bands at $3\,735$, $3\,710$, $3\,690$ and $3\,670\text{ cm}^{-1}$ (designated as bands 4–7 in Table II) are shifted by 80 – 90 cm^{-1} due to carbon monoxide adsorption. This shift corresponds to the proton affinity of OH groups equaling to $1\,420 \pm 20\text{ kJ/mol}$, which is close to the proton affinity of weak

acidic OH groups of aerosil⁸ (1 390 kJ/mol). These OH groups can be bonded to two or three aluminium cations and are thus bridge groups^{9,10}. Integrated intensities of individual OH bands of alumina are presented in Table II.

Aprotic acid centres. The presence of aprotic (Lewis) centres was indicated by the spectra of benzonitrile, pyridine and carbon monoxide. In the case of the pure alumina, the pyridine spectrum showed bands at 1 618, 1 580, 1 480 and 1 459 cm^{-1} which are typical for coordinated molecules⁵ (Fig. 2, curve 2a). The adsorption of benzonitrile led to formation of a band at 2 230 cm^{-1} corresponding to the physically adsorbed base and of another band at 2 287 cm^{-1} which can be assigned to the base coordinated to aluminium cation¹¹ (curve 4a). The carbon monoxide spectrum showed bands at 2 170 and 2 190 cm^{-1} (curve 3a). In accordance with literature^{6,12}, the band at 2 170 cm^{-1} corresponds to the carbon monoxide bonded to OH groups and the 2 190 cm^{-1} band can be ascribed to the carbon monoxide bonded to aluminium cations (Al^{3+}) which are arranged in defect octahedral coordination. Aprotic acidic centres conditioned by the Al^{3+} ions present in defect octahedral coordination have not been observed under dehydration conditions at 773 K, as documented by the absence of the CO band¹² in the 2 220–2 240 cm^{-1} region.

The total concentration of aprotic acidic centres (C_a) determined from the $\nu(\text{CO})$ band intensities with the use of reported data⁶ amounts to 2.7 $\mu\text{mol}/\text{m}^2$ for the alumina studied (Table III). This value agrees well with the concentration of aprotic acidic centres found for common alumina samples by combined IR spectroscopic and gravimetric method¹³: 1.5–5 $\mu\text{mol}/\text{m}^2$.

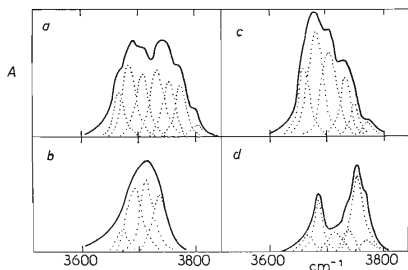


FIG. 1

IR spectra of surface hydroxyl groups of pure alumina a, $\text{Al}_2\text{O}_3 + 5\% \text{F}^-$ b, $\text{Al}_2\text{O}_3 + 5\% \text{SO}_4^{2-}$ c, $\text{Al}_2\text{O}_3 + 3\% \text{Na}^+$ d. Solid line designates the total spectrum, dashed line designates individual bands

Basic centres. The IR spectra of deuteriochloroform (Fig. 2, curve 1a) showed bands at 2 253 and 2 225 cm^{-1} ; separation of the spectrum revealed also the presence of a weak band at 2 240 cm^{-1} . The 2 253 cm^{-1} band can be ascribed to CDCl_3 complexes with weak basic centres⁷ (in the proton affinity scale, the strength of these centres $\text{PA} = 810 \text{ kJ/mol}$) which are likely hydroxyl groups. The 2 225 cm^{-1} band can be ascribed to CDCl_3 complexes with stronger basic centres ($\text{PA} = 895 \text{ kJ/mol}$) which are bridge oxygen atoms on alumina surface. The absolute concentration of basic centres has not been determined, since specific integrated intensity of $\nu(\text{CD})$ band on alumina is not known. The use of CDCl_3 as the probe made it possible to investigate for the first time in detail changes of the basic properties of aluminas modified by various ions.

TABLE II
Properties of OH groups

Band	1	2	3	4	4'
$\nu(\text{OH})$ band, cm^{-1}	3 803	3 780	3 756	3 735 \pm 10	
Proton affinity kJ/mol	1 590 \pm 25	1 590 \pm 25	1 590 \pm 25	1 420 \pm 20	1 310 \pm 20

Sample	Standard intensity of bands ^a					
Al_2O_3	1.42	11.0	10.3	14.6	0	
SO_4^{2-}	0.5	6.0	11.7	14.2	0	
1	1.3	9.2	9.4		10.3	
2	0.6	5.1	6.5		9.7	
3	1.3	5.8	10.4		12.3	
5	0.4	1.7	3.4	0		8.5
F^-	0.05	0.8	8.0	7.8	15.7	0
0.5	0.9	8.6	7.9	21.4		0
1	0	0.7	2.7		10.7	
2	0	0	7.1		15.4	
3	0	0	0	0		14.2
5	0	0	0	0		13.8
Cl^-	1.5	1.72	5.52	8.9		
Na^+	0.05	1.3	12.7	13.0	14.3	0
0.5	0	9.4	18.1	9.5		0
2	0	4.1	15.2	6.8		0
3	0	3.1	20.7	7.2		0
Zn^{2+}	1.5	1.3	12.7	9.6	15.4	0
Mg^{2+}	1	1.7	10.2	8.8	16.7	0

^a The intensity read from the spectrum, q tablet thickness, S sample surface.

The Effect of Anions

Hydroxyl groups. In Table II are summarized data on the effect of anions on alumina hydroxyl groups. The example of typical spectra is shown in Fig. 1, curves *b* and *c*. As in the intensities of hydroxyl groups, also some inhomogeneity in the sample preparation (drying conditions, calcination and thin plate forming) are reflected, the effect of ions on hydroxyl groups is discussed on the basis of relative intensities of individual bands with respect to the intensity of the total spectrum. The behaviour of OH groups assigned to bands 1–3 and 4–7 differs so much from each other that this deserves separate discussion. The dependence of relative intensities of individual high frequency bands 1–3 related to the total intensities of all the

TABLE II
(Continued)

5	5'	6	6'	7	7'
3 710 ± 10		3 690 ± 10		3 670 ± 10	
1 420 ± 20	1 310 ± 20	1 410 ± 20	1 310 ± 20	1 420 ± 20	1 310 ± 20
$A^* = 10^3 A/\rho S$ (relative units)					
13.2	0	16.0	0	7.8	0
12.9	0	19.3	0	11.9	0
	12.5		23.9	9.5	0
	9.3		12.5		8
	12.5		18.1		7.7
0	16.4	0	21.1	0	10
12.4	0	13.8	0	7.6	0
15.4	0	18.5	0	8.6	0
	11.7		11.9		5.6
	11.6		11.9		3.6
0	18.2	0	13.7	0	3.0
0	17.3	0	14.7	0	3.3
7.3		16.2		10.7	
14.3	0	21.1	0	10.4	0
7.4	0	16.3	0	6.5	0
6.8	0	15.7	0	5.0	0
7.7	0	13.0	0	4.9	0
14.0	0	16.5	0	7.9	0
10.0	0	19.0	0	5.12	0

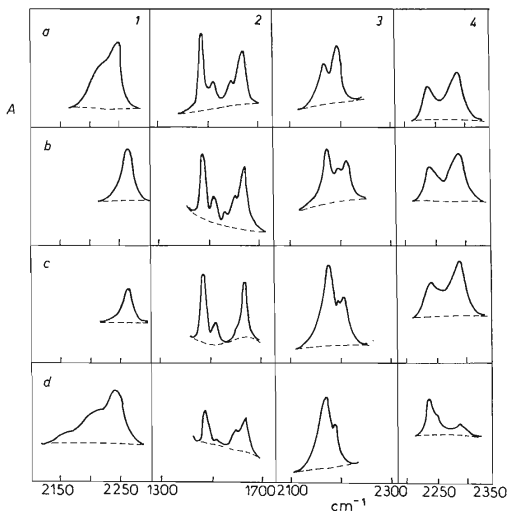


FIG. 2

IR spectra of deuteriochloroform 1, pyridine 2, carbon monoxide 3 and benzonitrile 4 adsorbed on the surface of pure alumina *a*, $\text{Al}_2\text{O}_3 + 5\% \text{F}^-$ *b*, $\text{Al}_2\text{O}_3 + 5\% \text{SO}_4^{2-}$ *c*, $\text{Al}_2\text{O}_3 + 3\% \text{Na}^+$ *d*

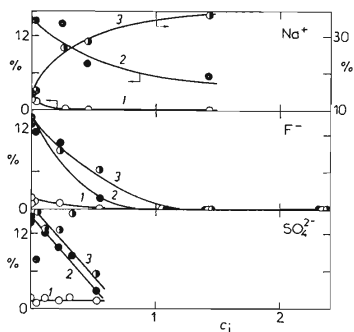


FIG. 3

Dependence of relative proportion of individual basic OH groups (%) in the total spectrum of modified aluminas on the amount of cations and anions c_i (mmol/g alumina). The hydroxyl group corresponding to the $\nu(\text{OH})$ band at $1\ 3\ 803\ \text{cm}^{-1}$, $2\ 3\ 780\ \text{cm}^{-1}$ and $3\ 3\ 756\ \text{cm}^{-1}$

bands upon concentration of added anions (expressed as mmol per g Al_2O_3) is shown in Fig. 3. The introduction of F^- results in essentially proportional decrease in the amount of all these groups and at the F^- content greater than 1 mmol/g Al_2O_3 these groups disappear. Sulphuric acid decreases substantially the concentration of OH groups ascribed to bands 2 and 3, the OH groups corresponding to band 1 and located on Al^{3+} cation surrounded by oxygen⁹ being affected only little. Chloride ions in the amount of 0.89% mass eliminate completely the OH groups corresponding to band 1 and the intensity of bands 2 ($3\,780\text{ cm}^{-1}$) and 3 ($3\,756\text{ cm}^{-1}$) decreases more than twice (Table II).

The effect of anions on the more acidic bridge OH groups corresponding to bands 4–7 is more complicated. Sulphate and fluoride ions change not only the OH group concentration but also their strength. In samples containing *c.* 3 to 5% mass of F^- , 5% mass of SO_4^{2-} ions, the $\nu(\text{OH})$ bands at $3\,735$ (band 4), $3\,710$ (band 5), $3\,690$ (band 6) and $3\,670\text{ cm}^{-1}$ (band 7) form hydrogen-bridged complexes with carbon monoxide which exhibit different shift $\Delta\nu(\text{OH})$; the complexes show $\Delta\nu(\text{OH})$ decrease by 150 cm^{-1} for F^- and by 140 cm^{-1} for SO_4^{2-} , which corresponds to the proton affinity of hydroxyl groups equal in average to $1\,310 \pm 20\text{ kJ/mol}$. In the region of lower anion concentrations, the surface contains likely also OH groups with proton affinity $1\,310 \pm 20\text{ kJ/mol}$ and the OH groups with proton affinity $1\,420 \pm 20\text{ kJ/mol}$, similarly as the starting alumina. For that reason, only changes in the total intensity of $\nu(\text{OH})$ bands due to added anions could be followed (Fig. 4, Table II). The introduction of F^- into alumina increased the proportion of OH groups corresponding to bands 4–6, that corresponding to band 7 being unchanged. The substantial changes in the proportion of strongly acidic OH groups ($\text{PA} = 1\,310\text{ kJ/mol}$) for fluoride concentrations 2–5% mass has not been observed. Sulphates in small amounts increase the proportion of OH groups corresponding to band 6 and decrease that corresponding to bands 5 and 4. On further increasing the amount of SO_4^{2-} ions in alumina, the proportion of OH groups characterized by the $3\,735\text{ cm}^{-1}$ band gradually decreases and the band 5 begins to increase. The intensity of the $\nu(\text{OH})$ band at $3\,690\text{ cm}^{-1}$ first decreases and then again increases. The introduction of Cl^- in amounts to 0.89% mass does not affect the intensity of $3\,690$ and $3\,670\text{ cm}^{-1}$ bands, whereas the intensity of $3\,735$ and $3\,710\text{ cm}^{-1}$ bands decreases, compared to the bands present in the spectrum of the pure alumina. The acidity of these OH groups does not increase significantly. Frequency shifts $\Delta\nu(\text{OH})$ for the complexes with carbon monoxide equal to *c.* 100 cm^{-1} , which corresponds to the proton affinity *c.* $1\,390 \pm 20\text{ kJ/mol}$.

Such a complex behaviour of OH bands can be explained by several factors. As it is seen from Table II, either the properties of some OH groups change without changes in their $\nu(\text{OH})$ (within experimental errors) and thus their proportion in samples changes or the frequency of OH groups of different acidity does change. As far as changes in $\nu(\text{OH})$ frequencies due to changes in OH group properties are

concerned, one can state that in accordance with recent data¹⁴ the acidic properties of OH groups and their $\nu(\text{OH})$ do not correlate with each other. Thus, for example, although different in acidity, acetic acid and halogeno derivatives thereof show the same $\nu(\text{OH})$ band at $3\,584\text{ cm}^{-1}$ in the gas phase. As the $\nu(\text{OH})$ value is affected mainly by the coordination sphere around the oxygen of OH group, one can expect that the effect of added ions on $\nu(\text{OH})$ would be slight, since with respect to oxygen, the ions would be present in the second coordination sphere. Therefore, changes in properties of OH groups can be judged only from the response to the action of molecules (probes) of defined properties, *i.e.* from $\Delta\nu(\text{OH})$.

Aprotic acidic centres. The introduction of SO_4^{2-} and F^- ions into alumina affects also aprotic acidic centres. In the IR spectrum of pyridine, one observes an increase in $\nu(\text{CC}(\text{N}))$ frequencies from $1\,618$ to $1\,623\text{ cm}^{-1}$ and somewhat smaller increase in the case of the $\nu(\text{CN})$ band of benzonitrile, *i.e.* from $2\,287$ to $2\,290\text{ cm}^{-1}$ (Table III, Fig. 2, curves *b* and *c*). These changes may indicate that the strength of aprotic centres is somewhat increased. This increase can be further deduced also from the spectra of adsorbed carbon monoxide. In the samples containing a great amount of anions, a new $\nu(\text{CO})$ appears at $2\,210\text{ cm}^{-1}$ (centres of type II, Table III and Fig. 5). According to reported data⁶, the strength of the centres corresponding to the CO adsorption characterized by the $\nu(\text{CO})$ band at $2\,210\text{ cm}^{-1}$ is approx. by 40 per cent greater than that of the centres of the starting alumina. Fig. 5 shows the dependence of the concentration of centres of type II and I on the amount of F^- and SO_4^{2-} ions. It becomes evident that the increase in the concentration of centres of type II is accompanied by the decrease in the concentration of centres of type I. One can therefore state that the introduction of anions leads to gradual transformation of centres of type I to those of type II.

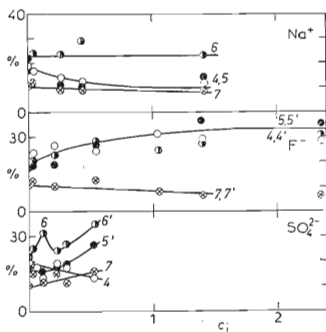


FIG. 4

Dependence of relative proportion of individual bands of different acidic OH groups (%) in the spectrum of modified aluminas on the amount of cations and anions c_i (mmol/g Al_2O_3). The hydroxyl group corresponding to the $\nu(\text{OH})$ band at 4, 4' $3\,735\text{ cm}^{-1}$; 5, 5' $3\,711\text{ cm}^{-1}$; 6, 6' $3\,690\text{ cm}^{-1}$; 7, 7' $3\,670\text{ cm}^{-1}$

TABLE III

Strength and concentration of aprotic Lewis acidic centres on the surface of pure and modified aluminas, determined by different spectroscopic probes

Sample	Carbon monoxide, $\nu_0(\text{CO}) = 2\,143\text{ cm}^{-1}$										Benzonitrile, $\nu_0(\text{CN}) = 2\,229\text{ cm}^{-1}$				Pyridine, $\nu_0(\text{CC}(\text{N})) = 1\,590\text{ cm}^{-1}$			
	I - Al ³⁺		II - Al ³⁺		III - Zn ²⁺		Al ³⁺		Mg ²⁺		Al ³⁺		Al ³⁺					
	$\Delta\nu$	A^{*a}	C_a^b	$\Delta\nu$	A^{*a}	C_a^b	$\Delta\nu$	A^{*a}	$\Delta\nu$	A^{*a}	$\Delta\nu$	A^{*a}	$\Delta\nu$	A^{*a}	$\Delta\nu$	D^{*c}		
Al ₂ O ₃	47	7.0	2.7	65	0	0	0	0	58	8.2	0	28	1.3					
	47	7.6	2.9	67	0	0	0	0	—	—	—	—	—					
SO ₄ ²⁻	48	7.2	2.8	67	0	0	0	0	—	—	—	—	—					
	2	49	5.4	2.1	67	0	0	0	—	—	—	32	1.13					
3	52	5.4	2.1	67	0	0	0	0	—	—	—	—	—					
	5	53	1.9	0.7	67	2.5	0.8	0	60	7.4	0	31	1.35					
F ⁻	47	6.1	2.4	65	0	0	0	0	—	—	—	—	—					
	50	6.8	2.6	65	0	0	0	0	—	—	—	—	—					
1	51	6.1	2.4	65	0.4	0.12	0	0	—	—	—	—	—					
	2	51	5.7	2.2	65	0.5	0.15	0	59	10.5	0	32	1.37					
3	51	3.9	1.5	65	5.4	1.62	0	0	—	—	—	—	—					
	5	51	3.2	1.2	65	3.8	1.14	0	61	7.7	—	31	1.23					
Cl ⁻	48	4.5	1.8	60	0.7	0.25	0	0	60	7.3	0	—	—					
	46	8.6	3.3	65	0	0	0	0	57	7.9	0	—	—					
Na ⁺	45	6.8	2.6	65	0	0	0	0	57	5.0	0	—	—					
	1	43	6.5	2.5	65	0	0	0	55	6.3	0	—	—					
3	37	4.9	1.9	65	0	0	0	0	54	3.1	0	25	0.97					
	47	6.7	2.6	65	0	0	60	0	—	—	—	—	—					
Zn ²⁺	46	7.5	2.9	65	0	0	60	0	—	—	—	—	—					
	2	45	7.5	2.9	65	0	60	0.4	—	—	—	—	—					
5	45	8.2	3.2	65	0	0	60	0.8	59	7.6	4.6	1.0	—					
	46	8.1	3.1	65	0	0	54	0	54	7.1	4.6	1.4	—					

^a $A^* = 10^3 A/\rho S$; ^b C_a — surface concentration in $\mu\text{mol}/\text{m}^2$; ^c $D^* = 10^3 D/\rho S$.

The introduction of Cl^- ions in amounts not exceeding 1% mass results in formation of aprotic acidic centres of type II. However, these centres are weaker than in the case of F^- and SO_4^{2-} ; $\Delta\nu(\text{CO})$ equals only to 60 cm^{-1} . Modification of alumina by chloride ions increases the strength of aprotic centres by 27 per cent, compared to the starting alumina. For this sample, the concentration of centres of type I amounts to $1.8\text{ }\mu\text{mol/m}^2$ and the concentration of centres of type II equals to $0.25\text{ }\mu\text{mol/m}^2$.

Basic centres. The introduction of anions to alumina exerts the most important effect on the properties of basic centres. Obtained data are summarized in Table IV and Fig. 6. The introduction of F^- and SO_4^{2-} ions causes above all the disappearance of the most basic centres with $\Delta\nu(\text{CD})$ of deuteriochloroform = 40 cm^{-1} (complex C); SO_4^{2-} ions added in $0.2\text{ mmol/g Al}_2\text{O}_3$ amounts nearly completely neutralize these centres. With F^- ion the same effect occurs at $1.5\text{ }\mu\text{mol/g Al}_2\text{O}_3$ concentration. Centres of types A and B are neutralized with greater difficulty. They disappear at SO_4^{2-} concentration $\sim 0.5\text{ mmol/g}$ and at F^- concentration equaling to approx. 2 mmol/g . The samples containing anions in greater amounts do not possess basic centres and the spectra of CDCl_3 exhibit only one $\nu(\text{CD})$ band at 2265 cm^{-1} (Fig. 2, curves 1b, 1c). As follows from reported data⁷, this band corresponds to the adsorption of CDCl_3 on acidic OH groups. The dependence of intensity of this band on the amount of added ions is presented in Table IV and Fig. 6. The intensity of this band can be used to determine the relative concentration of strongly protic centres in alumina.

The introduction of Cl^- ions into alumina (up to 1% mass) increases the concentration of centres of type A from 1.7 to 2.5 rel. units, which can be due to the fact that

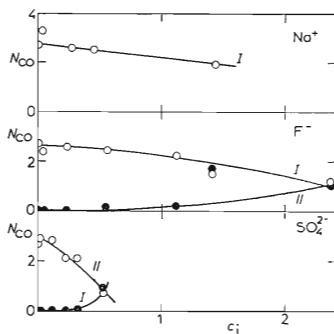


FIG. 5

Dependence of the amount of carbon monoxide adsorbed on aprotic centres N_{CO} ($\mu\text{mol/m}^2$) on the amount of cations and anions in modified aluminas c_i ($\text{mmol/g Al}_2\text{O}_3$). \circ Centres of type I, \bullet centres of type II

Cl^- ion can act as a weak basic centre. The centres on which CDCl_3 is adsorbed *via* its Cl atom, *i.e.* strong protic centres, are not formed on adding chloride ions in amounts about 0.8% mass.

Taking into account the above mentioned data, the effect of anions on alumina surface can be summarized as follows. The formation of stronger aprotic centres can be related to the fact that during dehydration a certain portion of OH groups moves from the Al^{3+} cation to which the introduced anions are coordinated. The effect of the strength of added acids reflects itself especially in the properties of basic centres. Thus, sulphates decrease the concentration of weak and strong basic centres

TABLE IV

Strength of different basic centres on the surface of pure and modified aluminas expressed as $\Delta\nu(\text{CD})$ and their relative concentration expressed as $\Delta^* = A/\rho S$

Sample	Type of complex and $\Delta\nu(\text{CD})$, cm^{-1}					
	A 12	B 25	C 40	D 57	E 110	H-band 0
Al_2O_3	1.7	1.4	4.8	0	0	0
SO_4^{2-} 0.5	1.3	1.4	2.2	0	0	0
1	0.8	1.3	0.4	0	0	0.4
2	0.4	0.8	0	0	0	1.4
3	0.3	0.2	0	0	0	1.8
5	0	0	0	0	0	2.1
F^- 0.05	1.5	1.3	4.4	0	0	0
0.5	1.4	1.3	1.6	0	0	0.8
1	1.3	1.2	1.2	0	0	0.9
2	0.6	0.4	0.2	0	0	1.5
3	0	0	0	0	0	2.9
5	0	0	0	0	0	2.4
Cl^- 1.5	2.5	0.6	0.5	—	—	—
Na^+ 0.05	1.9 (12) ^a	0	3.7	0.9	0	0
0.5	2.1 (15) ^a	0	3.0	1.6	0	0
1	2.8 (17) ^a	0	2.8	2.8	0	0
3	5.4 (25) ^a	0	0.6	4.7	0.9	0
Zn^{2+} 0.5	—	—	—	0	0	0
1.5	1.5 ± 0.2	1.5 ± 0.2	1.7 ± 0.2	0	0	0
3	—	—	—	0	0	0
5	—	—	—	0	0	0
Mg^{2+} 1	1.8	1.3	3.1	0.2 (65) ^a	0	0

^a $\Delta\nu(\text{CD})$ for the sample is given in parenthesis.

more than fluorides. The nature of these ions affects the concentration of different OH groups in the more complex way. To explain different behaviour of OH groups is very difficult, since the concentration of OH groups on surface at 773 K depends not only on their amount in the starting, completely hydrated sample but also on their thermal stability. The different behaviour of OH groups can be affected also by the topology of their distribution.

The Effect of Na^+ Ions

Hydroxyl groups. In Table II are summarized data on the effect of sodium ion on the hydroxyl groups of alumina. The IR spectrum of OH groups of the sample containing 3% mass Na^+ is represented graphically in Fig. 1d. Fig 3 shows the dependence of the relative intensity of the bands (expressed as the ratio of the intensities of individual bands to the total intensity of all the bands) of OH groups (bands 2 and 3) on the amount of Na^+ ions. The amount of OH groups characterized by band 1 decreases slowly upon introduction of 0.05% mass Na^+ and for the greater Na^+ concentrations this band disappears. The intensity of band 2 decreases strongly with increasing Na^+ concentration, whereas the intensity of band 3 increases. As the result of hydrogen bond formation with chloroform, band 2 at 3750 cm^{-1} shifts to the lower frequency region by $20\text{--}25\text{ cm}^{-1}$, which corresponds to the proton affinity $1540\text{--}1570\text{ kJ/mol}$. The portion of the acidic OH groups (bands 4–7) decreases after Na^+ ions are added (Fig. 4). The most distinct was the decrease in the intensity of band 4 (3735 cm^{-1}) and 5 (3710 cm^{-1}). The acidic properties of OH groups corresponding to band 6 did not change. Frequency shift $\Delta\nu(\text{OH})$ due to formation of hydrogen bond with CDCl_3 equaled to 40 cm^{-1} , which is close to the value for the pure alumina.

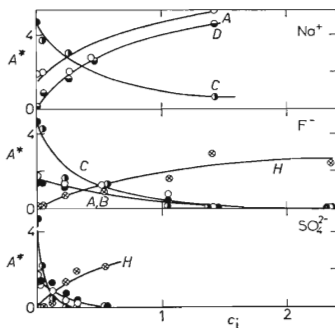


FIG. 6

Dependence of band intensities ($A^* = A/\rho S \cdot 10^3$ relative units) in the spectra of adsorbed deuterated chloroform on the amount of cations and anions in modified aluminas c_i (mmol/g Al_2O_3). \circ Complex of type A ($\nu(\text{CD}) = 2253\text{--}2240\text{ cm}^{-1}$), \bullet complex of type C ($\nu(\text{CD}) = 2225\text{ cm}^{-1}$), \blacksquare complex of type D ($\nu(\text{CD}) = 2208\text{ cm}^{-1}$), \odot H complex of acidic OH groups ($\nu(\text{CD}) = 2265\text{ cm}^{-1}$)

Aprotic acidic centres. Data obtained by the adsorption of carbon monoxide, benzonitrile and pyridine allowed to conclude that the presence of Na^+ ions decreases the strength of aprotic centres as well as their concentration (Table III). The spectra of molecules adsorbed on the sample containing 3% mass Na^+ are shown in Fig. 2 (curves 2d, 3d and 4d). Data presented in Table III document that the concentration of aprotic centres decreases from 2.7 to 1.9 $\mu\text{mol}/\text{m}^2$ and the strength, evaluated from $\Delta\nu(\text{CO})$, decreases approx. by 20 per cent. $\Delta\nu(\text{CN})$ for benzonitrile decreases from 58 for the pure alumina to 54 cm^{-1} and, similarly, $\Delta\nu(\text{CC}(\text{N}))$ for pyridine decreases from 28 to 25 cm^{-1} .

Basic centres. In Table IV are given data on the effect of Na^+ ions on basic centres of alumina. The spectrum of CDCl_3 adsorbed on alumina containing 3% mass Na^+ is shown in Fig. 2, curve 1d. The presence of Na^+ on alumina increases the concentration of centres of type A. At the same time these centres are also strengthened, since $\Delta\nu(\text{CD})$ increases from 12 cm^{-1} for alumina to 25 cm^{-1} for the sample containing 3% mass Na^+ . This value corresponds to the proton affinity increase (PA) from 810 to 860 kJ/mol. The concentration of basic centres of type C decreased from 4.8 to 0.6 relative units, which was accompanied by formation of new centres of type D having $\Delta\nu(\text{CD}) = 57 \text{ cm}^{-1}$. The increase in the concentration of centres of type D is parallel to the decrease in the concentration of centres C. One can assume that centres C are converted into centres D, *i.e.* the presence of Na^+ ions modifies properties of bridge oxygen atom. The sample containing 3% mass Na^+ possesses also stronger basic centres E with $\Delta\nu(\text{CD}) = 110 \text{ cm}^{-1}$, which corresponds to PA = 990 kJ/mol. Formation of centre E is caused likely by the oxygen which forms bridge between Na^+ and Al^{3+} cations. It seems likely that this centre is formed by substitution of the proton of the end OH group for Na^+ ion.

One can therefore conclude that the presence of sodium ion in alumina changes the strength of aprotic centres due to the effect of Na^+ ion *via* oxygen atom on the properties of Al^{3+} ion. Analogously to the effect of anions on acidic OH groups, also here the effect of Na^+ ions on the properties of basic OH groups is difficult to explain.

The Effect of Zn^{2+} and Mg^{2+} Ions

Data on the effect of Zn^{2+} and Mg^{2+} ions on the properties of alumina are presented in Tables I–III. The presence of these ions in alumina does not lead to changes in the hydroxyl groups of alumina. The strength and concentration of aprotic centres of the starting alumina (Table III) do not change, too. Only in the case of Zn^{2+} ion, the spectrum of carbon monoxide showed $\nu(\text{CO})$ band at 2203 cm^{-1} , the intensity of which was proportional to the amount of Zn^{2+} ion added. This band can be ascribed to the CO complex with surface Zn^{2+} ions. The effect of Zn^{2+} and Mg^{2+} ions on basic centres was also insignificant. The introduction of Zn^{2+} ions decreases the

concentration of basic centres of type C (Table IV) to the half in average; in the sample containing Mg^{2+} ion we observed formation of a centre giving complex with $CDCl_3$ having $\nu(\bar{C}D)$ $2\,200\text{ cm}^{-1}$. This centre can be attributed to formation of surface $Mg-O-Mg$ linkage; this cannot be, however, regarded as proved, since only one sample was measured.

By contrast to previous IR works, in the present study the analysis of acidic properties of modified aluminas was performed more systematically. The use of various molecular probes in IR measurements allowed to record changes in acidic properties of alumina samples and also to estimate the extent of these changes.

Application of Benesi Method

The results obtained by determination of the total acidity and strength distribution of acidic centres by Benesi method are presented in Table V. It was found that the total acidity of the pure alumina under measurement conditions equals to $2.1\ \mu\text{mol/m}^2$. The introduction of anions increased the total acidity by a factor of three

TABLE V
Partial and total acidity of modified aluminas determined by Benesi method

Sample	Partial acidities ^a , $\mu\text{mol/m}^2$				Total acidity, (a_i) $\mu\text{mol/m}^2$	
	a_1	a_2	a_3	a_4		
Al_2O_3		0.9	0	0	1.2	2.1
SO_4^{2-}	0.5	1.0	0.15	0	1.0	2.15
	1	1.1	0.2	0	1.35	2.65
	3	1.05	0.65	0.25	2.55	4.50
	5	1.30	0.9	0.5	2.5	5.2
F^-	1	1.1	0.65	0.45	0.7	2.9
	3	0.55	1.6	0.55	1.4	4.1
	5	2.6	0.75	0.10	1.1	4.55
Na^+	0.05	0.45	0.35	0.1	0.5	1.4
	0.5	0.1	0.3	0	0	0.4
	3	0	0	0	0	0
Zn^{2+}	1.5	1.2	0.05	0.05	1	2.3
	3	1.3	0.4	0	0.55	2.25
	5	0.8	0	0.3	1.2	2.3
Mg^{2+}	1	0.8	0.5	0.3	0.2	1.8

^a $a_1 - a_4$ are acidities ($\mu\text{mol/m}^2$) in the acidity region defined by Hammett acidity function H_0 : $a_1: 3.3 \geq H_0 \geq 1.5$; $a_2: 1.5 \geq H_0 \geq 5.6$; $a_3: -5.6 \geq H_0 \geq -8.2$; $a_4: H_0 \leq -8.2$.

and a certain acidity increase has also been observed after addition of Zn^{2+} ion. In contradistinction to this Group IIb cation, alkali metal (Na^+) or alkali earth ions (Mg^{2+}) decrease the total acidity.

The ions introduced into alumina affect not only the total acidity but change also the acidity distribution (Table V). While the pure alumina contained only weak and very strong acidic centres, alumina samples containing increased portion of SO_4^{2-} and F^- ions possessed greater portion of strongly acidic centres and, furthermore, also centres of medium acid strength. Cations in alumina (except Zn^{2+}) caused disappearance of acidic centres. On increasing Zn^{2+} content, the number of weak acidic centres decreased and the number of very strong acidic centres increased.

Qualitative analysis of the basicity of modified aluminas by adsorbed acid-base indicators showed that this method is not sensitive enough to characterize the basicity of aluminas used. It allowed only to detect the presence of very weak basic centres within Hammett acidity function H_0 region from 7 to 9.3, and that only for cation-containing aluminas. With the exception of the alumina containing 3% mass Na^+ , other samples did not show stronger basic centres with $H_0 > 9.3$. In the case of the sample containing 3% mass Na^+ , colour changes were observed with all the indicators having pK_a from 7.1 to 15.8, which means that the strongly alkalinized alumina contains a wide spectrum of basic centres, ranging from weak to very strong ones.

Correlation of IR Data with Data Obtained by Benesi Method

It was of interest to find whether there exists a relationship between IR data and data obtained by Benesi titration in nonaqueous medium, since Benesi method is frequently used to characterize acid-base properties of solid substances. We found a qualitative

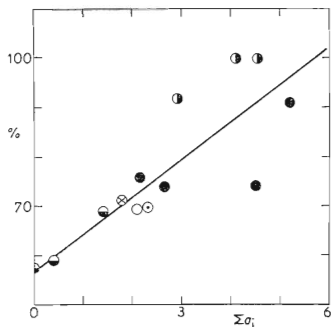


FIG. 7

Correlation of the relative proportion of acidic OH groups 4–7 in the total spectrum (%) with the total acidity of modified aluminas determined by Benesi method ($\mu\text{mol}/\text{m}^2$). \circ Al_2O_3 , \bullet $Al_2O_3 + SO_4^{2-}$, \bullet $Al_2O_3 + F^-$, \ominus $Al_2O_3 + Na^+$, \odot $Al_2O_3 + Zn^{2+}$, \ominus $Al_2O_3 + Mg^{2+}$

correlation of the total acidity determined by Benesi method with the portion of acidic OH groups (bands 4–7) in the spectrum of OH groups (bands 1–7). The correlation of both sets of data is shown in Fig. 7. With regard to the accuracy of data obtained, the correlation coefficient 0.83 supports this conclusion. The correlation of the proportions of individual OH bands with the acid strength distribution of centres has not been found. This fact is not surprising since the existence of such a correlation cannot be physically justified.

REFERENCES

1. Tanabe K., Shimazu K., Hatori H., Shimazu K.: *J. Catal.* **57**, 35 (1979).
2. Jirátořá K., Janáček L.: *Chem. Prům.* **31**, 174 (1981).
3. Benesi H. A.: *J. Phys. Chem.* **61**, 970 (1957).
4. Baliková M.: *Thesis*. Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, Prague 1972.
5. Kiselev A. V., Lygin V. I.: *Infrakrasnye Spektry Poverkhnostnykh Soedinenii*. Nauka, Moscow 1972.
6. Paukshtis E. A., Soltanov R. I., Yurchenko E. N.: *React. Kinet. Catal. Lett.* **16**, 93 (1981).
7. Paukshtis E. A., Kotsarenko N. S., Karakchiev L. G.: *React. Kinet. Catal. Lett.* **12**, 315 (1979).
8. Paukshtis E. A., Yurchenko E. N.: *React. Kinet. Catal. Lett.* **16**, 131 (1981).
9. Trochimets A. I., Mardilovich P. P., Lysenko G. N.: *Zh. Prikl. Spektrosk.* **30**, 873 (1979).
10. Knözinger H., Ratnasamy P.: *Catal. Rev.* **17**, 31 (1978).
11. Paukshtis E. A., Shinkarenko V. G., Karakchiev L. G.: *Kinet. Katal.* **17**, 1029 (1976).
12. Della Gatta G., Fubini B., Chiotti G., Mortherra C.: *J. Catal.* **43**, 90 (1976).
13. Nondek L.: *React. Kinet. Catal. Lett.* **2**, 283 (1975).
14. Bellamy L.: *Advances in Infrared Group Frequencies*. Methuen, London 1968.

Translated by J. Hetflejš.