

## THE EFFECT OF TITANIUM AND SODIUM IN ALUMINA ON ITS ACIDIC AND CATALYTIC PROPERTIES

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Acidic and catalytic properties of alumina containing small amounts of Ti(IV) and Na(I) (up to 1 wt. % of both) were examined. It has been proved that the amount of acid sites with the strength  $H_0 \leq 3.3$  and the initial reaction rates of cyclohexene isomerization depend linearly on calculated total electronegativity of the corresponding mixture of oxides.

For a long time, a great effort<sup>1-3</sup> has been devoted to the understanding of alumina surface, since its properties, like acidity and basicity, can play a significant role not only in the step of catalyst preparation by impregnation, but also when it is used as catalyst. As a rule, aluminium hydroxide prepared by precipitation from aluminate solution contains certain amount of sodium which is difficult to remove by washing. However, the presence of sodium in alumina has strong negative effect on the concentration and quality of surface acid sites and therefore on the course of catalytic reactions, like dehydration, isomerization, cracking, etc.

The aim of this work has been to find to which extent negative effect of sodium in alumina could be compensated by presence of titanium and acidic and catalytic properties of alumina be effected.

### EXPERIMENTAL

**Catalyst preparation.** Aluminium hydroxide containing various amounts of titanium dioxide and sodium monooxide was prepared by mixing of sodium aluminate solution with diluted nitric acid containing required amount of titanium tetrachloride at pH  $7.5 \pm 0.5$  and 50°C. The hydroxide was repeatedly washed by distilled water and samples of it were withdrawn after the eighth till twelfth washing steps, in order to obtain preparations with various content of sodium. They were dried in a drying box at 80°C for 24 h and calcined in a furnace at 550°C for 4 h. Denotation of samples and their chemical composition are given in Table I.

**Acidity determination** by Benesi method. The procedure of successive approximations was used<sup>4,5</sup>. The surface acidity was determined by titration with 0.05M solution of 1-butylamine in toluene using dimethyl yellow ( $pK_a$  3.3) as indicator. Prior to determination, the samples were ground to  $\leq 0.08$  mm particle size and activated by calcination in a furnace at 400°C for 2 h.

**Isomerization of cyclohexene.** All measurements were made with a fresh catalyst sample. Partial pressure of cyclohexene was 25 kPa, of hydrogen 75 kPa, temperature of reaction was

350°C. Products of reaction were analyzed by gas chromatography of the exit stream using a 5 m × 3 mm column packed with 15% Carbowax 1000 — Chromosorb P at 50°C and a catharometer as detector. The order of the reaction products emerging from the column was as follows: 2-methyl- and 3-methylcyclopentene, 1-methylcyclopentene, cyclohexene. Overall initial reaction rates were evaluated from the experimental dependence of conversion on reciprocal space velocity  $W/F$  as the slope at the origin.

*Surface area* was determined by BET method from adsorption of nitrogen at the temperature of liquid nitrogen, the contents of sodium and titanium were determined by atomic absorption spectrometry and of chlorine by titration using Volhard method.

## RESULTS AND DISCUSSION

Chemical analysis of samples given in Table I has shown that the content of chlorine is the same in two series of samples (0.05–0.06 wt. %). Therefore, it can be supposed that the effect of chloride ions on the surface and the catalytic properties of all

TABLE I

Denotation, chemical composition, and calculated electronegativity of samples

Sample	wt. %			Electronegativity $X_i$
	Ti	Na	Cl	
1.1	0	0.37	—	10.44
1.2		0.14	—	10.48
1.3		0.04	—	10.49
1.4		0.01	—	10.50
1.5		0.01	—	10.50
2.1	0.28	0.36	—	10.46
2.2		0.15	—	10.49
2.3		0.06	—	10.51
2.4		0.03	—	10.51
3.1	0.47	0.02	0.05	10.52
3.2		0.01	0.06	10.52
3.3		0.01	0.05	10.52
3.4		0.01	0.06	10.52
4.1	0.61	0.12	—	10.52
4.2		0.08	—	10.52
4.3		0.02	—	10.60
4.4		0.02	—	10.60
5.1	0.76	0.97	0.06	10.38
5.2		0.39	0.06	10.48
5.3		0.09	0.05	10.53
5.4		0.05	0.06	10.54

samples will be small and comparable in all series. Also surface area of the samples was found to be the same within the limits of measurement error –  $247 \pm 12 \text{ m}^2/\text{g}$ . The high amount of sodium in some samples has not influenced their surface area, very probably because of the relatively short time of calcination used.

The determined concentration of acid sites in alumina is shown in Fig. 1 in dependence on sodium concentration. In accordance with literature (*e.g.*<sup>6</sup>) the acidity increased with diminishing amount of sodium. Especially steep increase of acid sites was observed with samples in which sodium content was very low (0.05 to 0 wt. %). Fig. 1 demonstrates also that the presence of titanium in alumina increases the total acidity at all concentrations of sodium.

The effect of titanium on the acidity of alumina is seen from Fig. 2. Up to approximately 0.4 wt. % Ti, the acidity of alumina is practically constant. With further increase of titanium content, the total acidity increases nearly exponentially in the region 0.4–1 wt. % Ti. A similar trend for this concentration range was observed with samples of  $\text{TiO}_2\text{-Al}_2\text{O}_3$  which were prepared from  $\text{TiSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  by precipitation with urea<sup>7</sup>.

Tanaki and Ozaki in their work<sup>8</sup> showed that acid-base properties of solids are determined by induction effect of metal ions. They have obtained, for example, a linear correlation of isoelectric point of metal oxides with generalized electro-

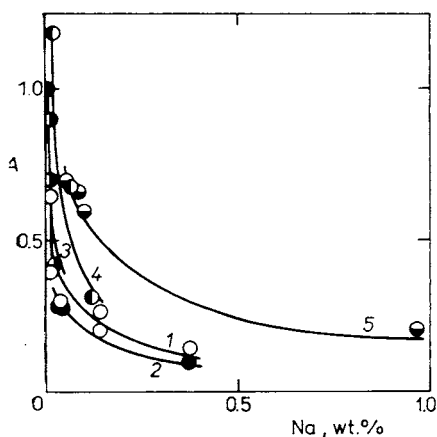


FIG. 1

The dependence of the total surface acidity  $A$  ( $\text{mmol g}^{-1}$ ) of various aluminas on the amount of sodium (wt. %) for various titanium content (Curve 1 (○) 0, 2 (●) 0.28, 3 (●) 0.47, 4 (●) 0.61, 5 (●) 0.76 wt. % Ti)

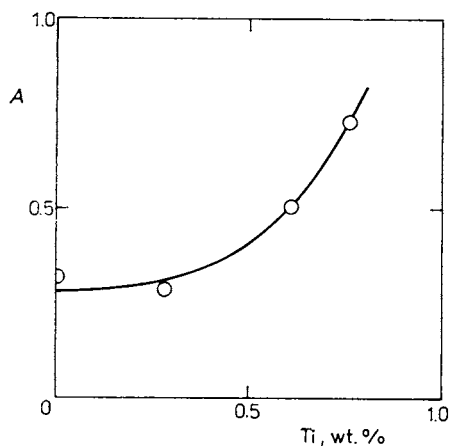


FIG. 2

The dependence of the total surface acidity  $A$  ( $\text{mmol g}^{-1}$ ) of aluminas on the amount of titanium content (concentration of Na = 0.05 wt. %)

negativity of metal ions  $X(\text{ion})$  calculated according to Sanderson<sup>9</sup> by the relation

$$X(\text{ion}) = (1 + 2Z) X_0, \quad (I)$$

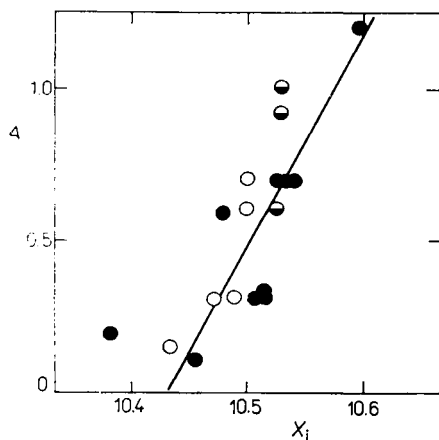


FIG. 3

The dependence of the total surface acidity  $A$  ( $\text{mmol g}^{-1}$ ) on the calculated electronegativity  $X_i$  of the mixture of aluminum oxide, titanium dioxide and sodium monoxide (( $\circ$ )  $\text{Al}_2\text{O}_3 + \text{Na}_2\text{O}$ , ( $\ominus$ )  $\text{Al}_2\text{O}_3 + \text{TiO}_2$ , ( $\bullet$ )  $\text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{Na}_2\text{O}$ )

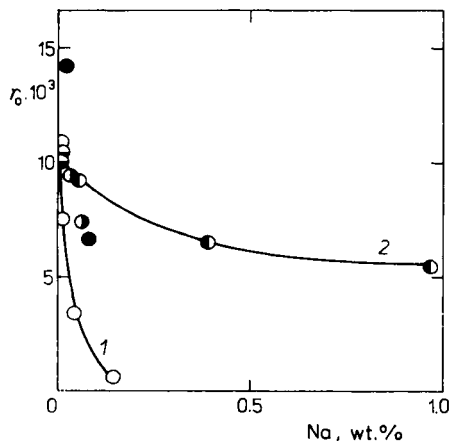
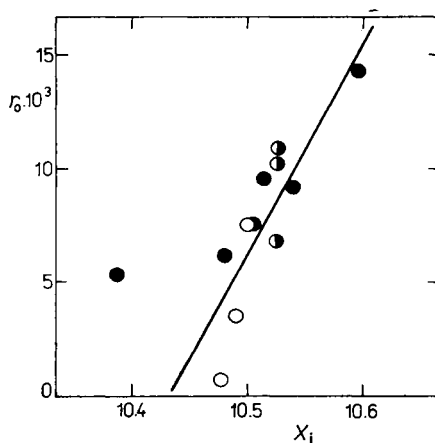


FIG. 4

The dependence of initial reaction rate  $r_0 \cdot 10^3$  ( $\text{mol h}^{-1} \text{g}_{\text{KAT}}$ ) of cyclohexene isomerization on the content of sodium in aluminas for various amount of titanium (Curve 1 ( $\circ$ ) 0, 2 ( $\ominus$ ) 0.76 wt. % Ti; for comparison further data are included ( $\oplus$ ) 0.28, ( $\omin�$ ) 0.47, ( $\bullet$ ) 0.61 wt. % Ti)

FIG. 5  
The dependence of initial reaction rate  $r_0 \cdot 10$  ( $\text{mol h}^{-1} \text{g}_{\text{KAT}}$ ) of cyclohexene isomerization on the calculated electronegativity  $X_i$  of mixture of aluminum oxide, titanium dioxide and sodium monoxide (( $\circ$ )  $\text{Al}_2\text{O}_3 + \text{Na}_2\text{O}$ , ( $\oplus$ )  $\text{Al}_2\text{O}_3 + \text{TiO}_2$ , ( $\bullet$ )  $\text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{Na}_2\text{O}$ )



where  $Z$  is charge of the ion and  $X_0$  electronegativity of metal given by Pauling.

Shibata and coworkers<sup>10</sup> have found correlation between the highest acid strength of equimolar binary mixtures of metal oxides and the arithmetic mean of electronegativity of corresponding couple of metal ions. It has been interesting to find out whether a relation exists between calculated electronegativity and total acidity of ternary mixtures of aluminium oxide, titanium dioxide, and sodium monooxide. Therefore, the electronegativities of  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{Na}_2\text{O}$  mixtures were calculated from the electronegativities of corresponding metal ions ( $X(\text{ion})$ ) under assumption of additive behaviour of this property and using molar fractions of the oxides ( $x(\text{oxide})$ ) as weights:

$$X_i = x(\text{Na}_2\text{O}) X(\text{Na}^+) + x(\text{TiO}_2) X(\text{Ti}^{4+}) + x(\text{Al}_2\text{O}_3) X(\text{Al}^{3+}). \quad (2)$$

From Fig. 3 it is seen that the dependence of total acidity of alumina containing various amount of titanium and sodium on the calculated electronegativity of the mixture of metal oxides is roughly linear. From this dependence we can estimate the value of total acidity  $0.5 \text{ mmol g}^{-1}$  for aluminium oxide without any ions (its electronegativity is 10.5). It is further obvious that the effect of sodium ion with electronegativity of 2.7 on the total acidity of alumina can be compensated by appropriate amount of titanium dioxide with electronegativity of 13.5.

Catalytic activity of alumina containing titanium and sodium was examined in isomerization of cyclohexene. In Fig. 4, the dependence of initial reaction rate of cyclohexene isomerization on the content of sodium in alumina is shown. It is seen that the presence of titanium significantly increases the reaction rate of isomerization. Also in this case, the initial reaction rate of isomerization has depended linearly on the electronegativity of corresponding mixture of metal oxides (Fig. 5). Further, a linear dependence of initial reaction rate of isomerization of cyclohexene on the amount of acidic sites with the strength  $H_0 \leq 3.3$  follows from Figs 3 and 5. Similar dependence was found in previous work<sup>11</sup>.

With respect to the found dependences, it would be interesting to find which type of acid sites and what distribution of acid strength will be generated in case of simultaneous presence of titanium and sodium in alumina. Up to now, the determination of protic and aprotic acid and base sites by IR spectroscopy was not successful.

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