TABLE 3 — SPECIFIC SURFACE AREAS (IN $m^2 g^{-1}$) OF GLASSY SILICA GEL AND FIBROUS SILICA GEL CONSIDERING PERPENDICULAR AND PARALLEL MODE OF ADSORPTION

Sorbate	Perpendicular mode of adsorption		Parallel mode of adsorption			
			A		B	
	Glassy gel	Fibrous gel	Glassy gel	Fibrous gel	Glassy gel	Fibrous gel
Diethylamine	593	60·6	754	77·6	1508	155·2
Di-*n*-propylamine	429	54·3	732	93·0	1464	186·0
Acetone	618	54·0	565	50·9	1130	101·8
Diethyl ketone	489	54·4	644	71·3	1288	142·6
Di-*n*-propyl ketone	391	52·6	679	91·4	1358	182·8

(A) One chain resting on the surface. (B) Two chains resting on the surface.

the parallel mode of adsorption, the molecule is considered as a rectangular rod[1]. Knowing the thickness of the hydrocarbon chain, the volume and the length, the molecular cross-sectional areas and hence the surface areas are found out. The surface areas thus calculated for both glassy and fibrous silica gels for the three modes of orientation are given in Table 3.

It is observed from Table 3 that the surface areas for fibrous silica gel calculated for only perpendicular adsorption are nearly the same. This indicates that the adsorption of secondary amines and ketones on the monolayer of fibrous silica gel is of oriented type and that these linear molecules are held perpendicular to the surface in the monolayer.

In the case of glassy silica gel, the surface area (calculated for perpendicular adsorption) with respect to di-*n*-propylamine is less than the value with respect to diethylamine. As far as the ketones are concerned, the value decreases in the order acetone > di-*n*-propyl ketone. This decrease in the surface area from the lower member to the higher member of the secondary amine and ketone series is similar to the behaviour of the different members of the normal aliphatic alcohols[1], normal aliphatic amines and aldehydes[2]. Adsorption of normal alcohols, amines and aldehydes on glassy silica gel has been concluded to be of mixed type, i.e. both perpendicular and parallel to surface. It follows that adsorption of the secondary amines and ketones on glassy silica gel must also be of the mixed type.

From the results obtained, it can be concluded that (i) the assumption of cross-sectional area of the secondary amine and ketone molecules as twice the cross-sectional area of the primary normal alcohols, amines or aldehydes is justifiable, (ii) adsorption of the secondary amines and ketones on the surface of glassy and fibrous silica gels is of oriented type, i.e. either perpendicular or parallel to surface or both, (iii) adsorption on the surface of fibrous silica gel is entirely of perpendicular type of adsorption, and (iv) adsorption on glassy silica gel surface is of mixed type, i.e. partly perpendicular and partly parallel to surface. These general conclusions are supported by the fact that glassy silica gel is microporous in structure and fibrous silica gel macroporous.

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Acidity & Catalytic Activity of Modified Zeolite-X

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Surface acidity and acid strength distribution of various forms of zeolite-X have been determined by non-aqueous titration technique. The activity for *o*-xylene isomerization has been found to depend upon the concentration of strong acid sites in the zeolite. Na-X contains only weak acid sites and is inactive whereas Ca-X and H-X possessing stronger acid sites are active for isomerization of *o*-xylene.

THE acidity of X-zeolites, which exhibit excellent acidic properties and possess carboniogenic catalytic activity[1-3] has been reported recently[4] but the acid strength distribution of decationated X-zeolites have not been studied so far. A complete description of acidic properties of a solid catalyst requires the determination of the nature of acid sites (Bronsted or Lewis type) as well as the acid strength distribution pattern. This communication presents our results on the determination of the acid strength distribution of decationated X-zeolites and their catalytic activity for *o*-xylene isomerization.

Linde 13 X (sample A) and 10 X (sample C) were commercial Union Carbide molecular sieves in powder form. The RRL-X (sample E) in Na-form was synthesized in our laboratory from paddy husk[5]. The ammonium forms of the zeolites were prepared by the conventional ion-exchange technique using an aqueous solution of NH_4NO_3 at 80°. The decationated samples G_1, G_2, G_3 and G_4 were prepared by subsequent heat treatment of the ammonium forms of Linde 13 X (sample G) at temperatures 380°, 500°, 600° and 750° respectively. Similarly sample I was a product of decationation of RRL-X (sample E). Pelletization was achieved by mixing the zeolite powder with a suitable quantity of a binder formulation developed in the laboratory. Thus, samples B, D, F, H and J were prepared from powder samples A, C, E, G_2 and I respectively. All the samples were finally calcined at 500° in air for 8 hr, unless otherwise specified.

Surface acidity and acid strength distribution were determined by carrying out non-aqueous titrations using *n*-butylamine as a base, benzene as a dispersant and Hammett indicators (Eastman Kodak or Aldrich) as the neutralization point detector[6,7]. The following indicators were used in this study: (i) *p*-Ethoxychrysoidin monohydrochloride ($pK_a + 5\cdot0$); (ii) N,N-dimethyl-*p*-phenylazoaniline ($pK_a + 3\cdot3$; wt % H_2SO_4, $3\cdot0 \times 10^{-4}$); (iii) 4-tolyl-azo-*o*-toluidine ($pK_a + 2\cdot0$, wt % H_2SO_4, $5\cdot0 \times 10^{-3}$); (iv) 1,9-diphenyl-1,3,6,8-nonatetraen-5-one ($pK_a - 3\cdot0$, wt % H_2SO_4, 48·0); (v) benzylidineacetophenone ($pK_a - 5\cdot6$, wt % H_2SO_4, 71·0); and (vi) anthraquinone ($pK_a - 8\cdot2$, wt % H_2SO_4, 90·0).

n-Butylamine and benzene were analytically pure and the latter was further purified by suitable treatments with sodium wire and activated silica gel.

Catalytic activity measurements were done at atmospheric pressure in a stainless steel reactor using gas chromatographic technique. A chrom-2 gas chromatograph equipped with flame ionization detector was used. The injection block was coupled with the reactor through swagelok tube fittings. A copper-column (6′×¼″) was packed with 10% triphenyl phosphate by weight on 60-80 mesh chromosorb P which was treated with acid washed hexamethyldisilizane. The column was operated at 80° using nitrogen as carrier gas.

For each experiment 2 g of zeolite sample (20-40 mesh) was placed in the reactor and dried by flowing nitrogen at 400°. The feed, chemically pure *o*-xylene, was obtained from Polyscience Corporation, USA and its purity was checked under experimental conditions. The reaction was studied by injecting a small amount of *o*-xylene to the reactor at 260°. The conversion was measured by determining the concentration of *o*-xylene and *m*+*p*-xylenes in the product.

The results on acidity measurements and catalytic activity for *o*-xylene isomerization are summarized in Table 1. The acid strength distribution spectrum of various zeolite samples indicates that both the sodium zeolites, viz. Linde 13 X and RRL-X (samples A and E), exhibit sites of only weak acid strength ($-3\cdot0 < pK_a \leqq +5\cdot0$). Replacement of sodium ions with calcium ions (sample C) not only increased the concentration of acid sites but also has generated fresh sites of medium ($-5\cdot6 < pK_a \leqq -3\cdot0$) and strong ($-8\cdot2 < pK_a \leqq -5\cdot6$) acid strength. These results are in agreement with those reported earlier by Hirschler[7].

When the sodium ions in Linde 13 X are replaced by ammonium ions and the samples heated to 380° to drive off NH_3, decationated product designated as H-X (H^+-form) is obtained. The concentration as well as the strength of acid sites has considerably improved by this treatment (compare samples A and G_1). On further increasing the calcination temperature the total concentration of acid sites reaches a maximum value at 500-600° and then declines. Calcination at 750° destroys the stronger acid sites completely, probably due to gradual structural degradation at higher temperature. The NH_4-X prepared from RRL-X on calcination at 500° also exhibits acidic properties similar to the decationated product of Linde 13 X (compare samples G_2 and I). It is evident from these findings that the maximum acidity is displayed by H-X zeolite formed by calcination of NH_4-X at 500-600°. Ward[2], on the basis of infrared spectroscopic studies of decationated faujasite type zeolites, has reported that the Bronsted acidity increases with calcination temperature up to about 325°, remains constant up to 500° and then decreases until at 800° it is about one-tenth of its maximum value. On the other hand virtually no Lewis acidity was observed until calcination temperature of 450°, but above 550° it increased rapidly as the Bronsted acidity decreased. Thus at about 500°, the zeolites are almost in Bronsted acid form and further increase

TABLE 1 — DIFFERENCE IN *n*-BUTYLAMINE TITRE VALUES (MMOLE/G) FOR INDICATORS OF DIFFERENT pK_a VALUES

Sample	$-3\cdot0 < pK_a \leqq +5\cdot0$	$-5\cdot6 < pK_a \leqq -3\cdot0$	$-8\cdot2 < pK_a \leqq -5\cdot6$	$\leqq -8\cdot2$	% conversion for *o*-xylene isomerization
A. Linde 13 X (Na-X), powder	0·30	0·0	0·0	0·0	—
B. Linde 13 X (Na-X), pellets	0·25	0·0	0·0	0·0	0·0
C. Linde 10 X (Ca-X), powder	0·10	0·20	0·05	0·0	—
D. Linde 10 X (Ca-X), pellets	0·10	0·15	0·05	0·0	6·0
E. RRL-X (Na-X), powder	0·30	0·0	0·00	0·0	—
F. RRL-X (Na-X), pellets	0·20	0·0	0·00	0·0	0·0
G. NH_4-X (from Linde 13 X), powder					
(1) 380°C (H-X)	0·15	0·20	0·05	0·0	—
(2) 500°C (H-X)	0·15	0·25	0·05	0·05	—
(3) 600°C (H-X)	0·16	0·25	0·05	0·0	—
(4) 750°C (H-X)	0·10	0·20	0·0	0·0	—
H. NH_4-X (from Linde 13 X), pellets	0·12	0·20	0·05	0·05	16·0
I. NH_4-X (from RRL-X), powder	0·10	0·20	0·05	0·05	—
J. NH_4-X (from RRL-X), pellets	0·10	0·15	0·05	0·05	12·0

in calcination temperature converts Bronsted acid sites to Lewis acid sites by the elimination of hydroxyl groups and formation of tri-coordinated aluminium atom[8]. On the basis of these arguments it can be inferred that the acidity measurements in the present investigation correspond to Bronsted acidity. Bronsted acid sites have been reported to be the active centres responsible for the carboniogenic activity[3].

A perusal of the activity data (Table 1) reveals that the pellets of Linde 13 X and RRL-X do not show any activity for *o*-xylene isomerization while the Linde 10-X brings about 6·0% conversion. The hydrogen forms of Linde 13 X and RRL-X exhibit 16 and 12% conversion respectively. The activity can be correlated with the data on the acid strength distribution. The sodium X exhibits only weak acid sites and, therefore, the % conversion for *o*-xylene isomerization is also negligibly small. In Ca-X some fresh strong acid sites are formed and so it shows a greater catalytic activity. In the decationated zeolite, H-X, not only the concentration of the total acid sites increases but some fresh very strong acid sites ($pK_a \leqq -8{\cdot}2$) are generated which are responsible for demonstrating a higher activity.

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Thermal Behaviour of Potassium Chlorate

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The thermal decomposition products of intimate mixtures of potassium chlorate and NiO, Cr_2O_3 and $K_2Cr_2O_7$ have been characterized by IR spectral measurements. The results suggest that the formation of potassium perchlorate during the decomposition of $KClO_3$ is probably due to the molecular rearrangement in the chlorate lattice.

ALKALI metal chlorates undergo thermal decomposition to give metal chlorides and oxygen[1-4]. A part of the chlorates also gets oxidized into the respective metal perchlorates during the decomposition. This may be due to the oxidation[2] of the undecomposed chlorate by the atomic oxygen produced during the decomposition or due to the molecular rearrangement of the chlorate lattice[4]. In this note thermal decomposition of potassium chlorate in the presence of Cr_2O_3,NiO and $K_2Cr_2O_7$ has been studied and a probable mechanism suggested employing thermogravimetric and infrared spectral studies.

Mixtures of 8:1 molar ratio of $KClO_3$ and Cr_2O_3, 2:1 molar ratio of $KClO_3$ and NiO, and 4:1 of $KClO_3$ and $K_2Cr_2O_4$ were prepared by taking the required amounts and grinding in an agate mortar for 10-15 min. Thermal decomposition studies were made in air using a Stanton recording thermobalance. After 60-70% decomposition of the samples, the thermal analysis was interrupted and the partly decomposed residues were subjected to infrared spectral analyses. The spectra were measured in the range 1300-620 cm^{-1} on a Perkin-Elmer 257 spectrophotometer using KBr pellet technique.

It is reported[5] that NiO and $K_2Cr_2O_7$ lower the decomposition temperature of $KClO_3$ from 400° to 300° and Cr_2O_3 not only lowers the decomposition temperature to 200° but chemically interacts to give $K_2Cr_2O_7$. The IR spectra of the partly decomposed $KClO_3$ obtained at 480° and that of 2:1 molar ratio of $KClO_3$ and NiO obtained at 340° are quite identical with absorptions around 1100 cm^{-1} due to $KClO_4$ and around 950 cm^{-1} characteristic of $KClO_3^6$. The spectrum of the partly decomposed 8:1 molar ratio of $KClO_3$ and Cr_2O_3 heating to 240°C exhibits bands around 950, 900, 870, 780 and 750 cm^{-1} which are characteristic of $K_2Cr_2O_7$ (ref. 6). No bands due to $KClO_4$ are observed. The spectra of the residues of 8:1 molar ratio of $KClO_3$ and Cr_2O_3 and that of 4:1 molar ratio of $KClO_3$ and $K_2Cr_2O_7$ obtained at 340° are identical and exhibit bands characteristic of $KClO_4$, $KClO_3$ and $K_2Cr_2O_7$.

Interaction of $KClO_3$ and Cr_2O_3 takes place in the temperature range 180-280° according to reaction (1)[5].

$$8KClO_3+3Cr_2O_3 \rightarrow 3K_2Cr_2O_7+2KCl+6ClO_2 \qquad \ldots(1)$$

If more than 8/3 moles of $KClO_3$ is present per mole of Cr_2O_3, the excess $KClO_3$ starts decomposing above 300°, on the other hand, if $KClO_3$ content is less than 8/3 moles per mole of Cr_2O_3, the excess Cr_2O_3 remains unoxidized. Chromium(III) oxide abstracts oxygen from the chlorate moiety and expels out chlorine dioxide, but there seems to be no oxidation of chlorate to perchlorate in the temperature range 180-300°. Potassium chlorate-chromium(III) oxide molar ratios less than 8:3 are introduced into the furnace at 320° and withdrawn immediately when the reaction just initiated. The residues are found to have infrared absorptions characteristic of $K_2Cr_2O_7$, $KClO_3$ and Cr_2O_3 with no absorptions due to $KClO_4$. The results suggest that the oxidation of potassium chlorate to perchlorate takes place above 300° in the presence of NiO and $K_2Cr_2O_7$ and above 400° in the absence of these substances.

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