

## Adsorption of Benzene & Cumene on NaX Zeolite & Its Scandium Forms at Low & High Temperatures

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Adsorption of benzene on NaX zeolite and scandium exchanged NaX zeolites has been measured by volumetric static system at 35°C. The adsorption capacity increases with increasing scandium content of the exchanged zeolite, reaching a maximum for the sample containing 6.46 wt% of scandium. The specific surface areas of the six samples have been calculated by BET equation. Adsorption of benzene and cumene on the different samples of zeolite has been studied by pulse chromatographic method, in the temperature range 250-400°C. The retention time ( $t_c$ ) and the retention volume ( $V_r$ ) of both the adsorbates on the six adsorbents have been calculated. The  $t_c$  and  $V_r$  values for cumene are higher than those for benzene throughout the temperature range. The values of  $t_c$  and  $V_r$  of both the adsorbates decrease with increase in temperature or increase in scandium content of the zeolite.

In an earlier investigation we reported the physical nature of the Russian NaX zeolite and of scandium exchanged NaX zeolites using X-ray, thermal differential analysis and BET  $N_2$  adsorption method<sup>1</sup>. In this paper are reported the results of the title investigation obtained using static volumetric system at low temperature and pulse chromatographic method at high temperature.

### Materials and Methods

NaX zeolite and scandium exchanged NaX zeolites were prepared as described earlier<sup>1</sup>. The samples of scandium exchanged NaX zeolites, viz. NaXSc<sub>1</sub>, NaXSc<sub>2</sub>, NaXSc<sub>3</sub>, NaXSc<sub>4</sub> and NaXSc<sub>5</sub> contained 3.70, 4.23, 6.45, 6.87 and 10.70 wt% scandium as revealed by colorimetric determination of scandium content of these samples<sup>1</sup>. Thiophene-free benzene and chemically pure cumene were further purified by standard methods. The adsorption isotherms of benzene at low temperature were obtained using the conventional volumetric static apparatus<sup>2</sup>. The pulse chromatographic system<sup>1</sup> was used to determine the adsorption of cumene and benzene at high temperature. Adsorbent (0.2 g) used was previously activated at 480°C in air for 4 hr then flushed with helium for 1 hr. The adsorbates, benzene and/or cumene were injected, in column packed with zeolite sample mixed with 10 cm<sup>3</sup> of quartz powder (particle diameter 0.25-0.5 mm). The microdose of the adsorbates was injected using helium as the carrier gas at constant flow rate (50 ml/min). The retention time,  $t_c$ , of the adsorbate in the adsorbent, i.e. the time recorded from the injection of the microdose to the maximum point obtained on the recorded peak, was determined and corrected for the dead space and the

space other than the packed length of the column. The retention volume,  $V_r$ , was calculated using Eq. (1) (ref. 3),

$$V_r = \frac{t_c F T_c}{m T_f} \frac{3}{2} \frac{\left(\frac{P_i}{P_o}\right)^2 - 1}{\left(\frac{P_i}{P_o}\right)^3 - 1} \quad \dots (1)$$

where  $t_c$  = the correct retention time ( $= t_{\text{obs}} - t_{\text{nitrogen}}$ ) in second;  $P_i$  = column inlet pressure (mm Hg) measured by manometer;  $P_o$  = column outlet pressure (mm Hg) at atmospheric pressure;  $F$  = carrier gas flow rate (ml/min) measured at  $P_o$  and  $T_f$ ;  $T_c$  = temperature of the column (K);  $T_f$  = temperature of the flow meter (K) and  $m$  = weight of the adsorbent (g).

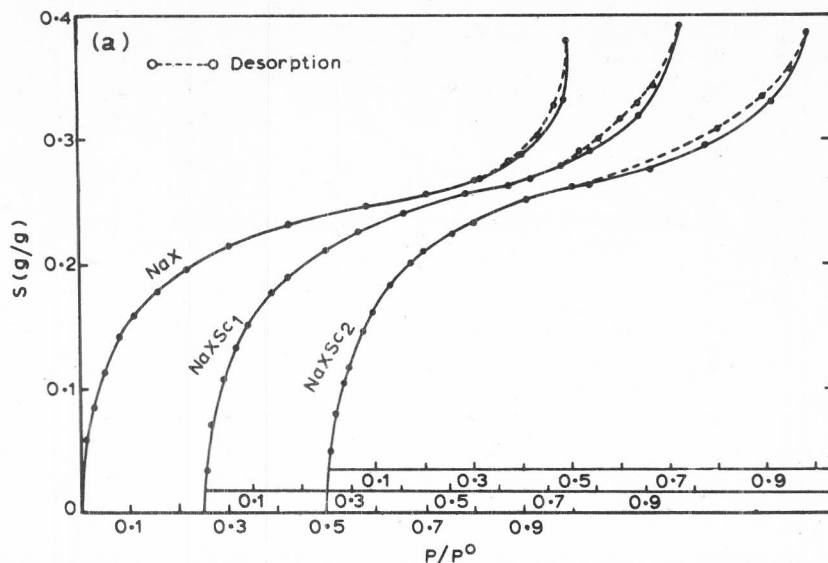
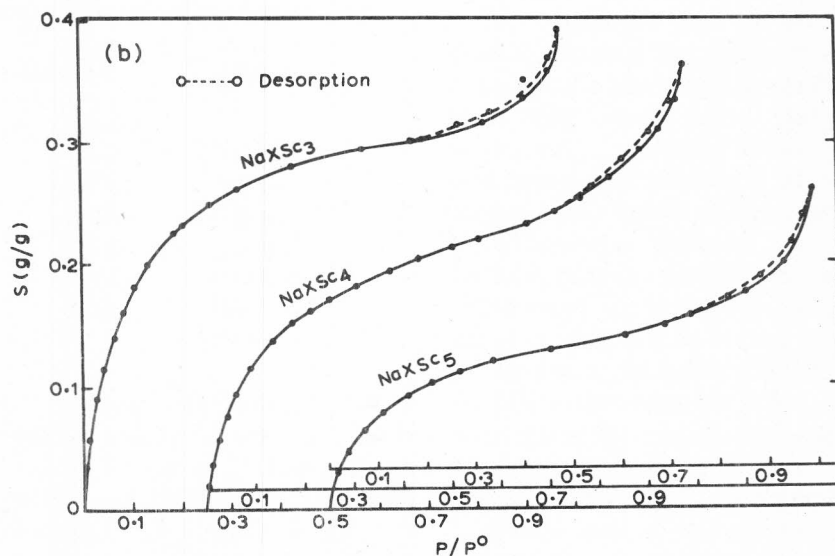
Making use of the retention volume, the heat of adsorption,  $\Delta H$  of the adsorbates was calculated<sup>3</sup> by Eq. (2)

$$\ln V_r = \frac{\Delta H}{RT} + C \quad \dots (2)$$

where  $V_r$  is retention volume per gram adsorbent;  $T$  is absolute temperature;  $R$  is universal gas constant and  $C$  is constant related to the entropy of adsorption, dimension of the column and the carrier gas flow rate.

### Results and Discussion

Adsorption of benzene vapour on NaX zeolite and its scandium exchanged NaX zeolites degassed at 400°C under reduced pressure ( $10^{-5}$  Torr) was studied at 35°C (Figs 1a and b). Adsorption of benzene on these adsorbents, was slow (3 to 4 days to attain equilibrium), particularly in the initial part of adsorption isotherm. At relatively higher vapour pressures ( $P/P^\circ > 0.1$ ) equilibrium was attained in

Fig. 1(a)—Adsorption of benzene at 35°C on NaX, NaXSc<sub>1</sub> and NaXSc<sub>2</sub> zeolitesFig. 1(b)—Adsorption of benzene at 35°C on NaXSc<sub>3</sub>, NaXSc<sub>4</sub> and NaXSc<sub>5</sub> zeolites

< 3 hr. The isotherms of benzene adsorption belong to Type-I of Brunauer classification<sup>4</sup>. Hysteresis was observed to occur for the adsorption of benzene on all the adsorbents, but the loops closed at about  $0.8 P^{\circ}$ . The adsorption capacity of benzene increased with increase in the scandium content in the exchanged NaX zeolite, reaching a maximum with the adsorbent containing 6.46% scandium. The adsorption isotherms were treated by BET equation, within the applicable range of the theory ( $P/P^{\circ} = 0.05-0.35$ ) and excellent linear plots were obtained from which the monolayer capacities,  $V_m$ , were determined. The results are given in Table 1 and Fig. 2.

Two values for the specific surface area were obtained, according to the vertical and horizontal

Table 1—Calculated Monolayer Capacities and Surface Areas of NaX Zeolite and Its Scandium Substituted Forms, from the Adsorption Isotherms of Benzene, at 35°C

Sample	$V_m$	Surface area ( $m^2/g$ ) at	
		$w_{vr} = 25 \text{ \AA}^2$ (ref. 5)	$w_{ft} = 45 \text{ \AA}^2$ (ref. 6)
NaX	0.1680	324	544
NaXSc <sub>1</sub>	0.1900	360	605
NaXSc <sub>2</sub>	0.1980	380	638
NaXSc <sub>3</sub>	0.2070	430	742
NaXSc <sub>4</sub>	0.1420	274	460
NaXSc <sub>5</sub>	0.0844	171	286

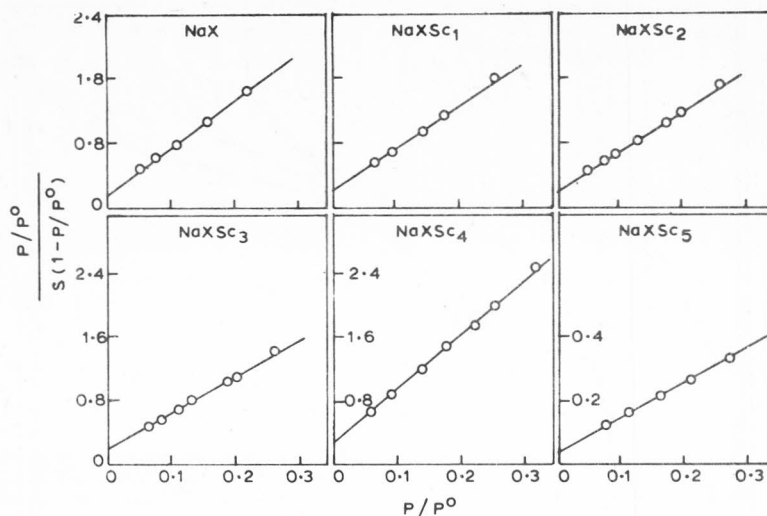


Fig. 2—BET plots of benzene adsorbed at 35°C on NaX, NaXSc<sub>1</sub>, NaXSc<sub>2</sub>, NaXSc<sub>3</sub>, NaXSc<sub>4</sub> and NaXSc<sub>5</sub> zeolites

orientation of adsorption of benzene molecules on the surface. They were different according to the cross sectional area assumed for the adsorbed benzene molecule. The values of specific surface area obtained according to the vertical and horizontal adsorption of benzene molecule were much lower than those obtained with nitrogen as an adsorbate<sup>1</sup>. This may be attributed to the specific interaction of benzene with the surface, a case which seldom occurs with nitrogen. The adsorption capacity, therefore, is related to the molecular area, molecular volume, orientation of the adsorbate molecules and the size of the pores of the adsorbent<sup>7</sup>. The polar nature of the surface in the micropores will considerably affect the orientation of the adsorbate. In wide pores, the polarization field will be diminished and benzene molecules will be adsorbed normally flat on the surface. The adsorbents employed in the present investigation are of very narrow pores, too narrow to accommodate more than one layer shared between two opposite surfaces. In such case, the area occupied by a molecule is expected to be twice that used in the calculation, namely, 50 Å<sup>2</sup>. It is of interest to point out that when the surface areas calculated assuming vertical orientation are multiplied by a factor of 2, this brings in most cases surface areas close to those obtained, from nitrogen adsorption<sup>1</sup> at -195°C, for the same adsorbents.

In view of the industrial importance of zeolite in petroleum refinery, adsorption of benzene and cumene using the pulse chromatographic system was studied in the temperature range 250-400°C on six adsorbent samples (0.2 g each) activated at 480°C.

The corrected retention time,  $t_c$ , as well as the retention volume  $V_r$ , of the two adsorbates with the adsorbents decreased with increase in temperature and increase in scandium content of the adsorbent. The original NaX zeolite has higher  $t_c$  and  $V_r$  than those

Table 2—Heat of Adsorption of Benzene and Cumene on NaX Zeolite and Its Scandium Exchanged Samples

Sample	$\Delta H$ kJ mol <sup>-1</sup>	
	Benzene	Cumene
NaX	66.88	70.22
NaXSc <sub>1</sub>	44.31	61.86
NaXSc <sub>2</sub>	44.31	55.18
NaXSc <sub>3</sub>	32.60	42.22
NaXSc <sub>4</sub>	27.59	30.93
NaXSc <sub>5</sub>	25.92	32.60

obtained with the scandium exchanged zeolites throughout the temperature range. However, in all cases  $t_c$  and  $V_r$  values of cumene were sufficiently higher than those of benzene. This may be attributed to the higher polarity of cumene (isopropylbenzene) relative to benzene<sup>8</sup>.

The heats of adsorption of benzene and cumene on NaX zeolite and its scandium exchanged samples in the temperature range 250-400°C are given in Table 2.

The heat of adsorption of benzene on NaX zeolite was calculated to be 66.88 kJ mol<sup>-1</sup>, from the linear plot of  $\ln V_r$  against  $1/T$ . This value is consistent with that obtained by Barrer and Eberly<sup>9-11</sup>. The heat of adsorption of cumene was higher than that of benzene on the same adsorbent samples. The heat of adsorption of both benzene and cumene decreased with increase in the scandium content of the adsorbent. The higher value of heat of adsorption of cumene than that of benzene may suggest that the former is more strongly adsorbed than the latter. The polarity of cumene may be responsible for such strong interaction of cumene with the surface of the adsorbent and for its relatively higher heat of adsorption.

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