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ALKALINE X AND Y ZEOLITES AS CATALYSTS FOR RING TRANSFORMATION: A TPD STUDY.

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ABSTRACT

Alkali cation-exchanged X and Y zeolites were prepared and tested as catalysts for the conversion of 2-methylfurane to 2-methylthiophene with hydrogen sulphide. The behaviour of the zeolites towards H_2S temperature programmed desorption was investigated. It seems to be related to the nature of the alkali cation and to the basicity of the framework oxygen atoms. The reaction selectivity towards 2-methylthiophene seems to depend among other factors, on the strength of the interaction between H_2S and the catalyst.

INTRODUCTION

The heterocyclic ring transformation reactions are very interesting because of the importance of the products as intermediates in fine chemicals manufacture. Among these reactions, the possibility of oxygen-sulfur exchange was reported by Venuto and Landis$^{(1)}$ while, more recently, ring transformation on zeolites has been investigated by Ono$^{(2)}$. No reports are found in the literature (to our knowledge) concerning the reaction between H_2S and 2-methylfurane (2MF) to give 2-methylthiophene (2MTF), which is an intermediate in pharmaceutical synthesis.

The behaviour of alkaline X and Y zeolites towards the H_2S adsorption and the catalysis of the reaction is presented here.

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EXPERIMENTAL

NaX an NaY were commercial products from Union Carbide (Na13X and LZY-52) while the Li, K, Rb and Cs exchanged samples were prepared following a well-known procedure(3). "Analythical grade" pure chemicals were used.

The TPD runs were performed in a conventional apparatus, equipped with a quartz microreactor (1 cm internal diameter) and a Philips thermocoax miniature thermocouple. A weighed amount of the sample (about 150 mg) was introduced in the reactor and activated in flowing He (40 cm^3/min.) during 12 hrs at 873 K (heating rate 10K/min.). After cooling down at 423K H_2S was admitted (6 cm^3/min.) and kept flowing for 1/2 hr. The sample was then purged in He (12 hrs at 423K, 40 cm^3/min.) before starting the TPD run (heating rate 10K/min., upper temperature limit 873K). The catalytic runs were performed in a continuous, fixed-bed microreactor described elsewhere(4) .

RESULTS AND DISCUSSION

The TPD spectra of H_2S are shown in Figures 1 and 2 for X and Y zeolites respectively, while information about the chemical composition of the samples is found in Table 1.

As Figure 1a shows, a big peak with a maximum at 573K is observed for NaX. Li, K, Rb and Cs-X zeolites have a similar peak (whose area is much smaller) with the maximum slightly shifted towards lower temperatures in the case of Rb and Cs. Moreover, another peak appears for all the samples, other than NaX, with the maximum at temperatures above 673K. When NaX zeolite is exchanged with the large cations Rb^+(r = 1.47Å) and Cs^+ (r = 1.69Å) the preferential localization of these ions are the sites III or IV within the supercage, and the ion exchange process is not complete(5). Moreover the "crowding" of these ions in the supercage forces the residual Na^+ ions from site II in the supercage to less well-defined sites at the walls of the ß-cages(6) . As a tentative interpretation we suggest that the first peak of the TPD spectrum of Rb,NaX and Cs,NaX is related to the presence of the residual Na^+ ions, while the big one comes from the presence of the Rb^+ and Cs^+ ions in the zeolite.

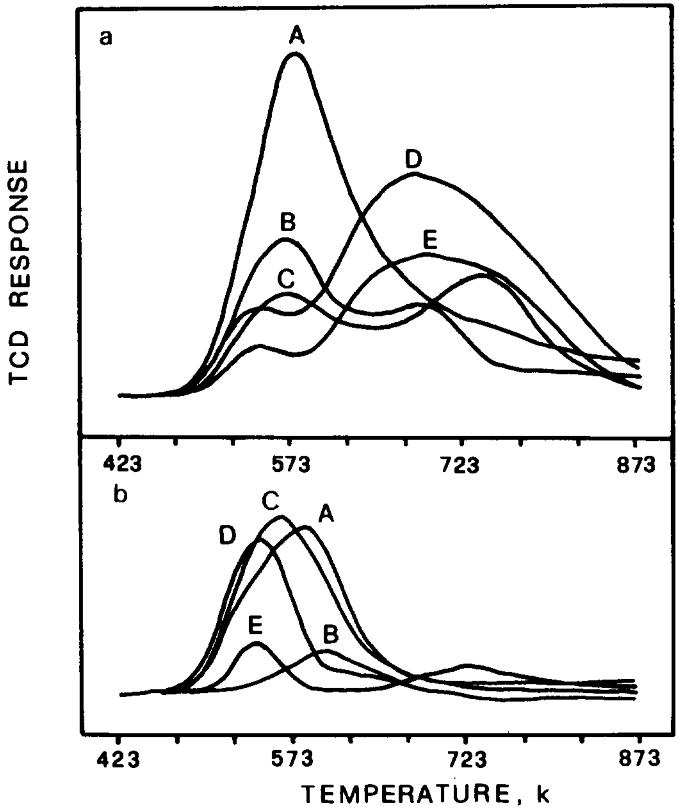

Fig. 1. TPD spectra for X(a) and Y(b) zeolites.
A,B,C,D,E refer to Na,Li,K,Rb and Cs forms respectively.

The slight shift towards lower temperatures of the maximum of the first peak could be due to the above cited crowding effect, which would weaken the interactions between H_2S and the residual Na^+ ions.

The high value of the second maximum for Rb,NaX and Cs,NaX (681K and 693K respectively) points out to strong interactions between these catalysts and H_2S.

When dealing with K^+ ions (r =1.33Å) the cation exchange process is much more efficient and involves the whole group of cation sites, even those in the smaller cavities (exagonal prisms, sites I). Both the weak and strong interactions (temperatures of the maxima at 573K and 746K respectively) observed in the TPD spectrum of K,NaX should then be related almost exclusively to K^+ ions.

The small dimensions allow also the lithium ion (r = 0.68Å) to exchange with sodium ions of any position. However, after the exchange process the amount of residual sodium ions is still high if compared to the amount of Li^+ present. A similar situation of cation excess has been reported for a lithium-exchanged X zeolite by Ziòlek(7), who related it to some deallumination of the framework. In this situation the contribution by the sodium and lithium ions cannot be distinguished.

TABLE 1

Chemical composition data, average oxygen charge (δ) and selectivity towards 2MTF (S_{2MTF}) for X and Y alkaline zeolites.

Sample	Residual Na (m equiv./g)	Me (m equiv./g)	I.E.[a] (%)	δ[b]	S_{2MTF}[c] (mol %)
Li, NaX	1.5	4.6	71	-0.396	38.5
NaX[d]	5.2	-	-	-0.399	60.4
K, NaX	0.4	4.6	92	-0.481	17.9
Rb, NaX	1.9	2.4	64	-0.439	55.1
Cs, NaX	1.0	1.8	82	-0.460	22.5
Li, NaY	1.5	2.5	61	-0.350	34.4
NaY[e]	4	-	-	-0.350	55.3
K, NaY	0.4	2.8	89	-0.379	69.2
Rb, NaY	1.1	1.9	73	-0.381	58.8
Cs, NaY	1.0	1.8	76	-0.394	50.6

(a) Ion-exchange degree respect to the original sodium form, (b) calculated as in reference(9), (c) at atmospheric pressure and 623K (d) Si/Al=1.4, (e) Si/Al=2.4.

The H_2S desorption from Y zeolites is shown in Figure 1b. All the TPD curves, except the one for Cs,NaY, exhibit just one maximum, whose position is shifted towards high temperatures in the order Li>Na>K>Rb.

In the case of Cs,NaY two peaks are observed, one at 541K and the other (very small and enlarged) at 733K.

A plot of the amount of H_2S adsorbed (as measured by the total area under each TPD curve) vs. the average oxygen charge, for X zeolites calculated according to(8), is shown in Figure 2a.

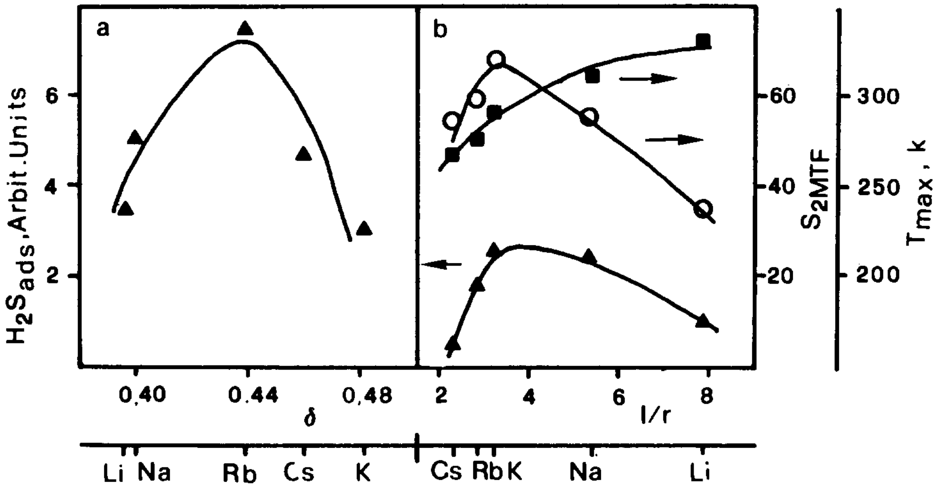

Fig. 2. a: H_2S adsorbed vs. average oxygen charge for X zeolites. b: H_2S adsorbed (▲), 2MTF selectivity (○) and T_{max} (■, external scale of ordinates) vs. I/r for Y zeolites.

It can be seen that an increase of the average oxygen charge (i.e. the basic character of the framework(9)) influences the adsorption, which reaches a maximum and then decreases. This suggests the occurrence of a dissociative adsorption of H_2S on X zeolites. This has been observed also by Karge and Raskò(6) by means of the IR technique. It is likely that under our experimental conditions a non dissociative mechanism is super-imposed for X zeolites, as already reported for similar systems by Ziòlek(10). A plot of the amount of H_2S adsorbed on Y zeolites vs. the electron acceptor capacity of the cations

I/r(11) is shown in Figure 2b. It can be seen that the amount of H_2S reachs a maximum and than decreases for the smaller cations, i.e. when the cation accessibility becomes lower. Moreower, as the electron acceptor capacity increases a shift towards higher temperatures of the maximum of the TPD curves is observed (see Figure 2b), which points out to the expected increase of the strenght of the interaction. This suggests that a non-dissociative mechanism is prevalent.

For Y zeolites, the selectivity variation with I/r follows the same trend observed for the amount adsorbed, as shown in Figure 2b. The selectivity decrease for the small cations seems steeper than the corresponding decrease of the amount adsorbed, which reveals the effect of the strength of interaction. Strong evidence for the influence of this latter is obtained when X and Y zeolites are compared. Thus although the amount of H_2S adsorbed is almost the same on K,NaX and K,NaY the selectivity value for the former is 17.9% while K, NaY is very selective (69.2%). Looking at the corresponding TPD curves we can see, however, that in the case of K,NaX, very strong interactions are involved.

CONCLUSIONS

The adsorption of H_2S on alkali cation exchanged-X zeolites depends on the basic character of the zeolite framework, while on Y zeolites it is related to the electron-acceptor capacity of the cation. The selectivity of the reaction of 2-methylfurane to 2-methylthiophene is influenced by the strenght of the interactions between H_2S and the catalyst.

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