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Evidence for non-site-isolation in ZSM-5 from ion-exchange and catalytic studies

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Ion exchange of HZSM-5 samples with alkali metal cations, using metal chloride solutions, results in partially exchanged zeolites, MHZSM-5, M = Li, Na, K or Cs. The degree of exchange is found to increase with increasing ionic radius of the cations. The catalytic properties of the alkalized zeolites were evaluated using the reaction conditions under which the catalytic activity of the HZSM-5 samples in terms of n-hexane cracking is proportional to the aluminium content. From the residual catalytic activity exhibited by the Na-, K- and CsHZSM-5 samples it is concluded that each of the larger Na^+, K^+ and Cs^+ ions is influencing more than one AlO_4^- tetrahedron, implying that the aluminium sites in ZSM-5 are not isolated. The ion-exchange results are then interpreted in terms of non-isolated aluminium sites. The ion-exchange and catalytic properties of the zeolites as a function of aluminium content are also discussed.

Keywords: ZSM-5; ion-exchange; alkali metal cations; n-hexane cracking; catalytic test reaction

1. Introduction

Partially poisoned ZSM-5 zeolites, with alkali metal cations, have found application as catalysts for some acid-catalyzed reactions [1–3]. In a recent publication we reviewed the ion-exchange properties of this zeolite [4]. In that paper we also reported on the ion exchange of HZSM-5 with potassium ions (using potassium chloride solutions) and on the accompanying implications for the catalytic properties of the alkalized zeolites. It was observed that (i) only partial exchanges could be achieved, (ii) in the aluminium range used, the degree of exchange decreased with increasing aluminium content, and (iii) from

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a study of the catalytic properties of the partially exchanged zeolites, using n-hexane cracking as the catalytic test reaction (CTR) and the reaction conditions under which for the HZSM-5 samples *the percentage conversion is shown to be proportional to the percentage aluminium* [5,6], the zeolites exhibited considerably lower catalytic activities than those expected from the degree of exchange achieved.

We have now examined the effect of other alkali metal cations such as Li^+, Na^+ and Cs^+ both on the ion-exchange behaviour of HZSM-5 and on the catalytic properties of the MHZSM-5 samples, M = Li, Na, K or Cs. Furthermore, these properties were examined as a function of the aluminium content of the zeolites.

2. Experimental

The ZSM-5 samples were prepared according to previously documented methods [4,7] from the system $3Na_2O$-2TPABr-xAl_2O_3-$20SiO_2$-$1000H_2O$ in stirred autoclaves (Parr) at 150 ° C for 72 hours. At the end of the hydrothermal treatment, the solid product was extensively washed with distilled water until the filtrates were free of bromide ions, as detected by the addition of silver nitrate to the filtrates. The samples were then calcined at 630 ° C in air for 3.5 hours, exchanged with 1 M NH_4Cl solutions three times at room temperature, and then washed with distilled water in order to remove the chloride ions. The H^+-form of the zeolites was then obtained by calcination of the NH_4^+-form at 550 ° C for 3 hours. All samples were found to be highly crystalline as determined by XRD [8] and a catalytic test reaction [9]. The number appearing after "ZSM-5", e.g. HZSM-5/90, denotes the SiO_2/Al_2O_3 ratio of the batch as calculated from the amounts of silica and aluminium hydroxide used in the syntheses.

For the ion-exchange experiments, 10 ml of the metal chloride solution were used per gram of zeolite. The reactions were allowed to proceed with stirring at 25 ° C for 20 hours [4]. After filtration, the solids were extensively washed with distilled water until they were free of chloride ions. The elemental analyses of the solids were determined by atomic absorption after acid digestion of the solids.

The catalytic experiments were carried out in a stainless steel tubular reactor with an internal diameter of 15 mm [10] using 0.200 g of zeolite diluted with 3.7 g of quartz (Merck). Nitrogen at 20 ml/min was flowed through the saturator, containing n-hexane and maintained at 0 ° C [11], and then over the catalyst bed. The extent of n-hexane conversion at 500 ° C and at 20 min on-stream was monitored by on-line analysis of the products using gas chromatography (FID, Poropak R column).

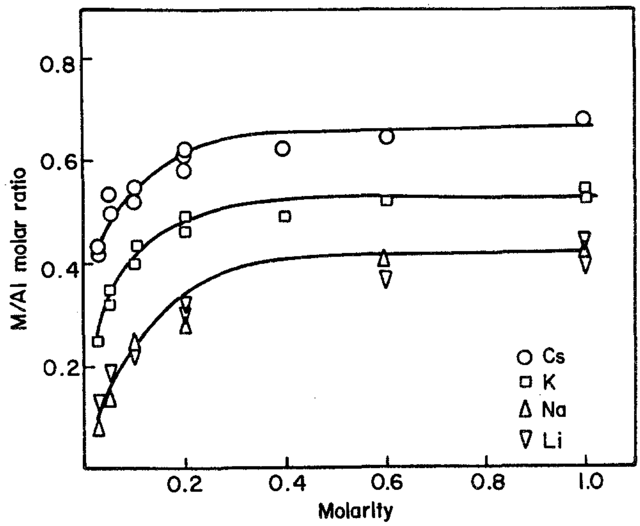

Fig. 1. Plot of M/Al molar ratios versus molarity of the MCl solutions, M = Li, Na, K or Cs, for sample HZSM-5/90.

3. Results and discussion

Using batch HZSM-5/90, we examined the degree of exchange of the H^+-form of the zeolite as a function of the molarity of the solution for the four cations Li^+, Na^+, K^+ and Cs^+ (using metal chloride solutions). The results obtained are shown in fig. 1. With all four types of cation and up to a molarity of approximately 0.2, an increase in the degree of exchange is observed after which it remains essentially constant. From the plateau values of the isotherms it can be concluded that, with increasing hydrophilicity of the ions (see table 1) the degree of exchange decreases [4,12], with Li^+ and Na^+ giving approximately identical results. As reported previously [4,5], higher degrees of exchange of HZSM-5 with alkali metal cations can be achieved under more "forcing" conditions.

Table 1
Hydrated and ionic radii of the alkali metal cations [1] and the $[Al/M^+]_{cat.}$ and $[Al/M^+]_{exch.}$ ratios [2]

Cations	Hydrated radii (Å)	Ionic radii (Å)	$[Al/M^+]_{cat.}$	$[Al/M^+]_{exch.}$
Cs	3.29	1.69	1.5	1.5
K	3.31	1.33	1.5	1.8
Na	3.58	0.95	1.2	2.4
Li	3.82	0.60	0.92	2.4

[1] Taken from ref. [12].

[2] For sample MHZSM-5/90.

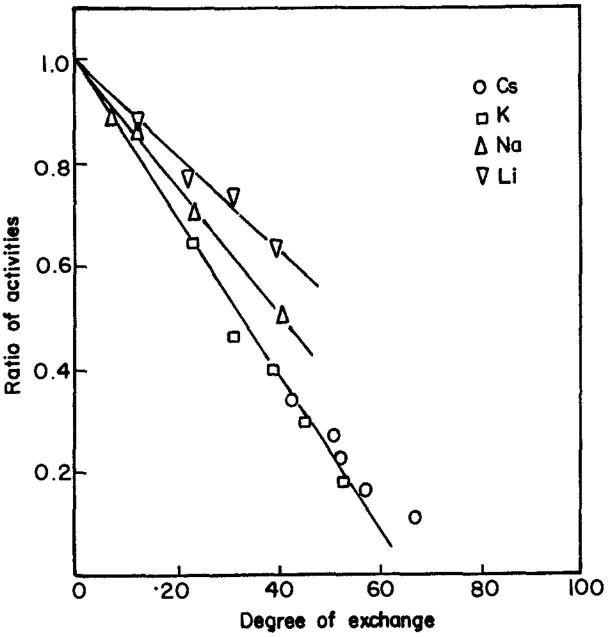

Fig. 2. Plot of the ratio of activities (MHZSM-5/HZSM-5, M = Li, Na, K or Cs) versus degree of exchange.

The catalytic properties of the above MHZSM-5 samples were then evaluated in terms of n-hexane cracking as CTR, using the reaction conditions under which the catalytic activity of the HZSM-5 samples is proportional to the aluminium content [4,13]. The results, plotted in terms of the ratio of the activities (activity of MHZSM-5/activity of HZSM-5) versus the degree of exchange, are shown in fig. 2. As expected, and for all four cations, the ratio of the activities decreases with increasing degree of exchange. Most significantly, though, the rate of decrease is clearly a function of the type of cation, or more precisely, the size of its ionic radius (see table 1). Thus, at the same exchange levels, e.g. 40%, we see that with the smaller (in terms of ionic radius) lithium ions, the residual activity is considerably higher, whereas with the larger ions, cesium and potassium, the residual activity is considerably lower. From the above two figures, it is therefore obvious that during ion exchange of HZSM-5, the hydrophilicity of the ions is the dominant factor influencing the level of exchange, whereas in terms of residual catalytic activity, the ionic radii are more important [14].

From an extrapolation of the lines in fig. 2, the intercept can give us the theoretical exchange level needed for each cation in order to achieve zero conversion. From these values it is then possible to calculate the effective number of aluminium sites influenced by each cation, i.e. to determine the catalytic Al/M^+ ratio (or $[Al/M^+]_{cat.}$). These ratios are 0.92 for Li^+, 1.2 for

Na^+ and 1.5 for K^+ and Cs^+ (table 1). Thus, the $[Al/M^+]_{cat.}$ ratio, or effective degree of poisoning, at least in terms of n-hexane cracking as CTR and under our reaction conditions, increases with increasing ionic radius of the alkali metal cations. However, since (i) the rates of decrease exhibited by the K- and CsHZSM-5 systems are equal, even though the ionic diameter of Cs^+ is greater than that of K^+ by 0.72 Å, (ii) the aluminium sites in ZSM-5 are probably located at the larger channel intersections [15–18], and (iii) the reaction is carried out at the relatively high temperature of 500 ° C [19], it can be concluded that the decrease in catalytic activity observed with the MHZSM-5 samples, M = Na, K or Cs, is not due to diffusional constraints imposed by the presence of the alkali metal cations. The results therefore suggest that each of the larger sodium, potassium and cesium cations is influencing more than one AlO_4^- tetrahedron, implying that the aluminium sites in ZSM-5 are not isolated. Furthermore, the results for the lithium samples show that with this small cation the decrease in activity is approximately proportional to the degree of exchange. This demonstrates that the catalytic activity is due to ion-exchangeable acid sites [20].

A further conclusion that can be drawn from the results shown in fig. 2 is that there is an almost total loss of catalytic activity with the samples exchanged with 1 M KCl or CsCl solutions. This strongly suggests that the degrees of exchange obtained with these 1 M solutions are the maximum values obtainable under our exchange conditions due to the fact that $[Al/M^+] < 1$, which is of course in agreement with the observed levelling-off of the isotherms in fig. 1. These values therefore allow us to calculate the ion-exchange Al/M^+ ratios (or $[Al/M^+]_{exch.}$), i.e. the effective number of AlO_4^- tetrahedra influenced by each alkali metal cation during ion exchange. Assuming the same holds for the other two cations (viz. lithium and sodium), the $[Al/M^+]_{exch.}$ values for ZSM-5/90 are then 2.4 for both Li^+ and Na^+, 1.8 for K^+ and 1.5 for Cs^+. In other words, each cation influences more than one aluminium site, with the exchange ratio increasing with increasing hydrophilicity of the cation (lithium and sodium giving the same results).

The above $[Al/M^+]_{cat.}$ and $[Al/M^+]_{exch.}$ ratios refer, of course, only to sample MHZSM-5/90. The ion-exchange properties, using 1 M solutions, of a series of samples in which the aluminium content ranged from 0.2–1.6% by mass (corresponding to SiO_2/Al_2O_3 ratios of 540–60) were also examined and the results obtained with each of the cations are shown in fig. 3. With varying aluminium content and up to 1% by mass, the levels of exchange for all four cations remain essentially constant but, as expected, decrease with increasing hydrophilicity of the cations. Beyond the 1% level, it was found that the degrees of exchange decrease with increasing aluminium content. Even when the molarity of the solutions was increased to 2 M, identical degrees of exchange were obtained.

The above results suggest that up to 1% aluminium, the highly hydrophilic

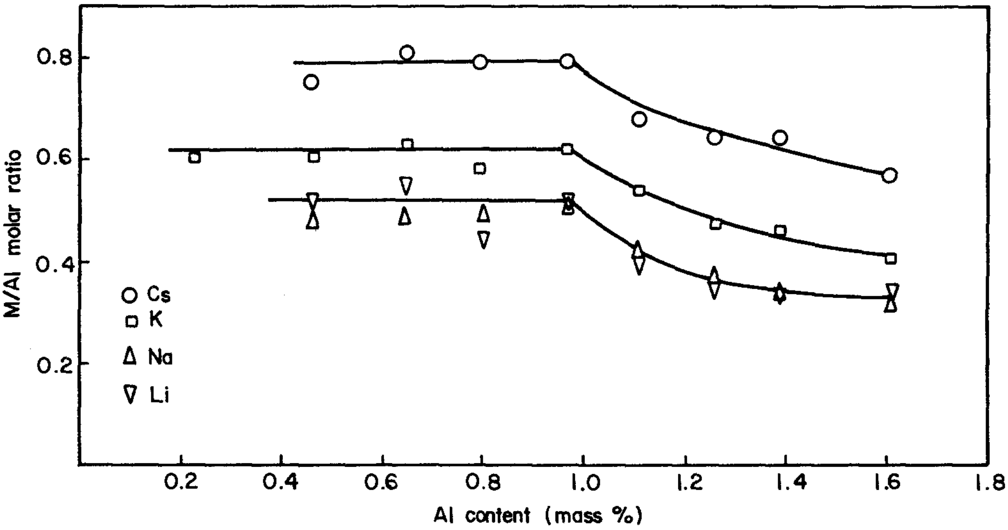

Fig. 3. Plot of M/Al molar ratios (M = Li, Na, K or Cs) versus aluminium content of the zeolites.

cations, Li^+ and Na^+, are influencing two aluminium sites (i.e. $[Al/M^+]_{exch.} = 2$) whereas with the smaller cesium ion, for example, the corresponding ratio is 1.3. Within this aluminium range, therefore, it appears that the AlO_4^- tetrahedra are probably in NNN positions [20,21], with each lithium or sodium cation influencing both of them. Thus, due to their large hydrated radii, two sodium or lithium ions are unable to neutralise two acid sites when the latter are in NNN positions. A further implication of our results is that even at the lower aluminium contents, the AlO_4^- tetrahedra occur preferentially in pairs. As the aluminium content increases beyond 1%, the $[Al/M^+]_{exch.}$ increases to 3 for lithium and 1.8 for cesium. The results strongly suggest that, at the higher aluminium contents, as many as three aluminium sites are occurring in NNN positions.

The catalytic properties of some of the samples shown in fig. 3 were also evaluated and the results are listed in table 2. In agreement with the results shown in fig. 2, all the CsHZSM-5 samples, irrespective of aluminium content,

Table 2

Ratio of activities of MHZSM-5/HZSM-5 samples as a function of aluminium content [1]

SiO_2/Al_2O_3	Li	Na	K	Cs
60	0.66	0.61	0.33	0.14
80	–	0.64	0.29	0.11
110	0.65	0.44	0.24	0.07
180	0.48	0.38	0.26	0.12
270	0.44	0.32	0.23	0.16
540	–	–	0.24	–

[1] M = Li, Na, K or Cs.

exhibit low residual activities. However, these activities were considerably higher for the LiHZSM-5 samples. The results are in agreement with our previous conclusions that during catalysis, the ionic radius of the cations is the important parameter influencing the resultant catalytic activity of the partially exchanged zeolites. Furthermore, the results show that with the cations having large hydrated radii, higher residual activities were obtained with increasing aluminium content. It may therefore be concluded that at the higher $[Al/M^+]_{exch.}$ values (that is, at high aluminium contents and with the ions having large hydrated radii) insufficient shielding of the active sites is taking place during the catalytic reaction, resulting in the observed higher residual activities (relative to those obtained with the samples of low aluminium content).

4. Conclusion

The combination of the results obtained from our ion-exchange studies (partial exchanges) and catalytic studies (almost total loss of catalytic activity under the specific reaction conditions) on HZSM-5 and MHZSM-5 offers us sufficient evidence to conclude that the aluminium sites in zeolite ZSM-5 are not isolated but occur in clusters of two or three depending on the aluminium content. From the results obtained with the LiHZSM-5 samples, it may also be concluded that even though the sites are not isolated, they appear to exhibit equal catalytic activities.

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