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TEMPERATURE-PROGRAMMED DESORPTION OF METHYLNAPHTHALENE FROM ALKALI-METAL FAUJASITES

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Interaction between 1-methylnaphthalene and alkali-metal X and Y zeolites has been investigated using TPD. All spectra show only a single peak, the temperature of which changes with the nature and amount of the alkali-metal cation and the Si/Al ratio of the faujasite. A correlation between peak temperature and average charge of structural oxygen atoms of the zeolite is shown. On the basis of the atomic charge distribution in the 1-methylnaphthalene molecule, it is suggested that adsorption is initiated by interaction between the alkali-metal cation and the carbon atom of the methyl group. Simultaneously, an interaction involving hydrogens atoms of the aromatic rings and structural oxygen atoms of the zeolite occurs, except for X samples containing high amounts of large alkali-metal cations.

Keywords: temperature programmed desorption, zeolite

Introduction

The interaction between aromatic hydrocarbons and synthetic zeolites is of great interest because of the widespread application of these solids as selective adsorbents and catalysts. Among aromatics, 2-methylnaphthalene (2MN) and 2,6-dimethylnaphthalene (2,6DMN) are particularly valuable as intermediates in fine chemistry [1]. The use of zeolites is economically attractive for either the separation or these components from alkylnaphthalene mixtures of the catalytic isomerization of 1-methylnaphthalene (1MN) and dimethylnaphthalenes into 2MN and 2,6DMN respectively. The possibility of upgrading polynuclear aromatic feedstocks by this route has been tested in our laboratory [2–6], but little attention has been paid to the nature of the interactions in methylnaphthalene–zeolite systems.

In this investigation the interaction between 1MN and alkali-metal faujasites has been studied by means of the thermal-programmed desorption (TPD) technique.

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Experimental

Zeolites

NaX and NaY were commercial products from Union Carbide (Na13X and LZY52). They were exchanged under reflux for two hours at 368 K with the appropriate chloride solutions to prepare the Me^INaX and Me^INaY samples at maximum ion-exchange. Partially exchanged CsNaX samples were obtained by treating NaX at 298 K for 12 h with 0.05, 0.1 and 0.5 *N* CsCl. 'Analytical grade' pure chemicals were used. Chemical compositions of the samples, obtained by atomic absorption analysis after $HF–HClO_4$ attack, are reported in Table 1.

TPD runs

A conventional apparatus, equipped with a quartz microreactor (1 cm i.d.), a Philips thermocoax miniature thermocouple and thermal conductivity detector was used. A weighted amount of the sample (about 50 mg) was introduced into the reactor and activated in flowing He (40 cm^3/min) for 12 h at 823 K (heating rate 10 deg·min^{-1}). After cooling at 523 K the sample was saturated by injecting small pulses of 1MN until saturation. The sample was then purged in He (6 h at 523 K, 40 cm^3/min) before starting the TPD run (heating rate 10 deg·min^{-1}, temperature limit 873 K).

Table 1 Characteristics of the zeolites employed

Sample	Chemical composition	δ_O^a
$Li_{55}Y$	$Li_{55}(AlO_2)_{55}(SiO_2)_{137}$	–0.347
$Na_{55}Y$	$Na_{55}(AlO_2)_{55}(SiO_2)_{137}$	–0.349
$K_{39}NaY$	$K_{39}Na_{16}(AlO_2)_{55}(SiO_2)_{137}$	–0.371
$Rb_{26}NaY$	$Rb_{26}Na_{29}(AlO_2)_{55}(SiO_2)_{137}$	–0.381
$Cs_{25}NaY$	$Cs_{25}Na_{30}(AlO_2)_{55}(SiO_2)_{137}$	–0.394
$Li_{80}X$	$Li_{80}(AlO_2)_{80}(SiO_2)_{112}$	–0.390
$Na_{80}X$	$Na_{80}(AlO_2)_{80}(SiO_2)_{112}$	–0.399
$K_{70}NaX$	$K_{70}Na_{10}(AlO_2)_{80}(SiO_2)_{112}$	–0.438
$Rb_{38}NaX$	$Rb_{38}Na_{42}(AlO_2)_{80}(SiO_2)_{112}$	–0.435
$Cs_{35}NaX$	$Cs_5Na_{45}(AlO_2)_{80}(SiO_2)_{112}$	–0.460
Cs_5NaX	$Cs_5Na_{75}(AlO_2)_{80}(SiO_2)_{112}$	–0.404
$Cs_{12}NaX$	$Cs_{12}Na_{68}(AlO_2)_{80}(SiO_2)_{112}$	–0.411
$Cs_{26}NaX$	$Cs_{26}Na_{54}(AlO_2)_{80}(SiO_2)_{112}$	–0.424

[a] Average charge on oxygen atoms.

Results and discussion

TPD spectra of 1MN from the Me^{I}NaY and Me^{I}NaX samples (Me^{I} = Li, Na, K, Rb and Cs) are shown in Fig. 1. All the curves show only a single peak. The peak temperature changes along the series Li–Na<K<Rb<Cs for the Me^{I}NaY catalysts (Fig. 1A), whereas this order is reversed for the Me^{I}NaX zeolites (Fig. 1B). Substitution of Na^+ ions of the parent $Na_{80}X$ by increasing amounts of Cs^+ ions causes the peak temperature to move to lower values (Fig. 1C).

The desorption behaviour of a catalyst is related to the nature of the interaction between the adsorbed molecule and the solid. The system benzene–zeolites has been widely investigated by means of different techniques. According to Primet *et al.* [7], C_6H_6 is adsorbed on Y zeolites through the formation of a π complex with cations in the S_{II} position, located near the centre of the hexagonal window. Formation of such a complex has been confirmed by Fitch *et al.* [8]. They report that a benzene molecule can be also located in the middle of the window formed between adjoining supercages by 12 tetrahedral atoms and 12 bridging octahedral atoms. The window has a free diameter of about 7.5 Å and thus providing an ideally-sized site for adsorption of a benzene molecule. De Mallmann and Barthomeuf [9–11] have shown that the hydrogen atoms of the aromatic and structural oxygen atoms are involved in this phenomenon. According to these authors the distribution of benzene between the two modes of adsorption (cations in the supercage and 12-R oxygens) is governed by the acid–base character of the zeolite.

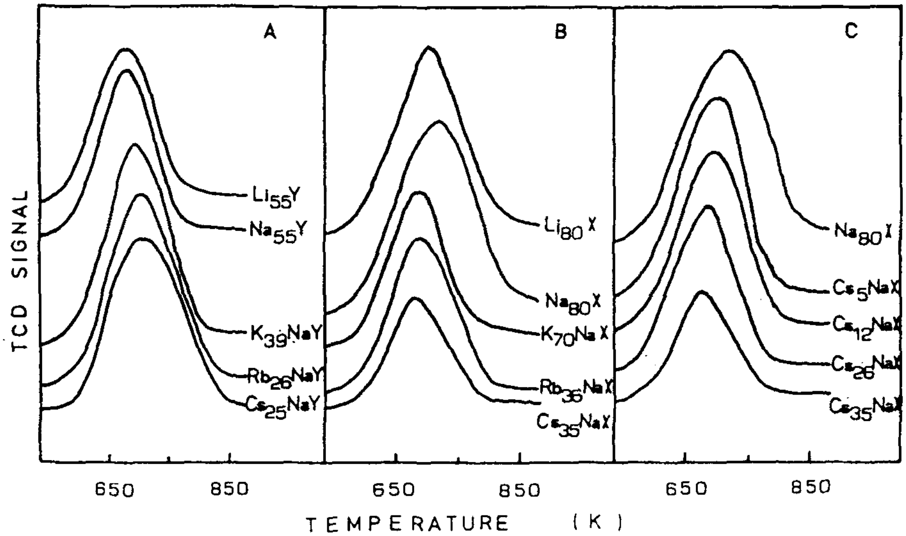

Fig. 1 TPD spectra of 1-methylnaphthalene from alkali-metal faujasites. (A) and (B), Me^{I}NaY and Me^{I}NaX at highest ion exchange, respectively. (C), CsNaX samples with increasing Cs^+ content

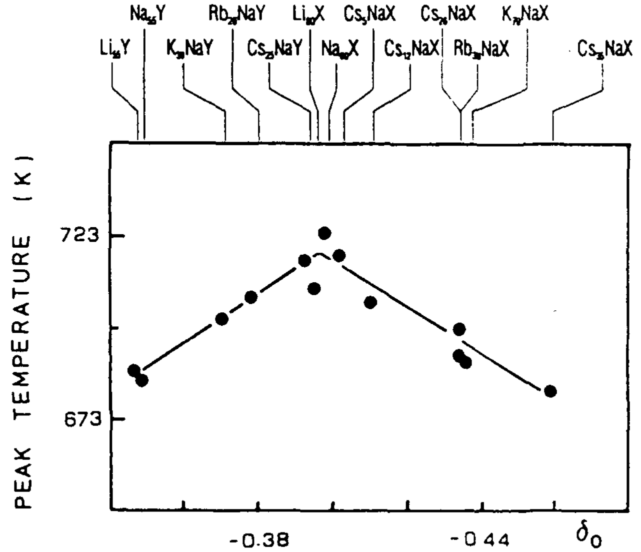

Fig. 2 Peak temperatures in TPD spectra of 1-methylnaphthalene from alkali-metal faujasites *vs.* negative charge of structural oxygen atoms, δ_0

Straightforward application of this model to our system is not possible. The presence of two condensed aromatic rings makes formation of the π complex difficult, as the dimensions of the aromatic molecule do not correspond to those of the cationic site. Even less likely is the possibility of adsorption in the 12-R window, as this is too small to suitably accommodate the large 1MN molecule.

Some indication of the positions within the 1MN molecule which could be involved in the adsorption process can be obtained by considering values of the net charges on each carbon and hydrogen atom of the 1MN molecule. Calculations were performed following Ref. [12] for both 1MN and benzene. The charge distribution on 1MN is not symmetrical as with benzene. For the former the highest negative charge (–0.1811) is associated with the carbon atom of the methyl group, the other C atoms having charges in the range –0.0563 to –0.1286. The hydrogen atoms of 1MN rings bear, in any case, a positive charge higher than that of hydrogen atoms in benzene. Bearing this in mind an interaction mechanism between the carbon atom of the methyl group and the alkali-metal cations in the zeolite supercage can be suggested. Should this be the only kind of interaction determining adsorption, the strength of the latter would depend on the electrostatic potential of the alkali-metal cation. However, the structural oxygen atoms could also play a role. The planar part of the 1MN molecule could still rotate to some extent on the C_1–CH_3 bond and this would allow some of the hydrogen atoms of the rings to interact with structural oxygen atoms in suitable positions, particularly if these carry a high (negative) average charge. According to this scheme the alkali-metal ions should be responsible for initiating the adsorption, which would be stabilized if interaction with structural oxygen atoms could take place.

The average oxygen charge, δ_o, has been calculated for our samples according to Ref. [13] from the following formula:

$$\delta_o = (S_{int} - 5.21) / 4.71 \qquad (1)$$

where S_{int} is the intermediate electronegativity of the zeolite. The relevant values, listed in Table 1, were used to obtain the plot of peak temperature *vs.* δ_o shown in Fig. 2. The expected increase of adsorption strength (represented by the peak temperature) with δ_o is observed up to $Na_{80}X$. Further increase of the average oxygen charge does not result in strengthening of the adsorption, in fact it gets weaker particularly for the Rb- and Cs-exchanged X-zeolites. It would seem that the structural oxygen atoms are not involved in the adsorption, the strength of which would therefore be determined only by interaction with the alkali-metal cations, *i.e.* particularly low for those exerting a low electrostatic field (Rb^+ and Cs^+). Thirty and 44 Na^+ ions are located in the supercage of $Na_{55}Y$ and $Na_{80}X$ respectively according to Ref. [14]. It is well known [15] that ion-exchanging NaX samples with the large Rb^+ and Cs^+ ions causes crowding in the supercage; this does not occur for Y zeolites with low cation populations in the supercage. This crowding of large cations in the supercage is strongly dependent on the degree of ion-exchange and could hinder possible interaction between structural oxygen atoms and hydrogen atoms of 1MN. As expected, the peak temperature decreases along the series $Na_{80}X<Cs_5NaX<Cs_{12}NaX<Cs_{26}NaX<Cs_{35}NaX$, although δ_o increases.

Conclusions

An explanation of the strong adsorption of 1MN on alkali-metal faujasites is proposed. The alkali-metal cations are assumed to initiate the adsorption by interacting with the carbon atom of the CH_3 group, while structural oxygen atoms interact with hydrogen atoms of the aromatic rings. The latter interaction cannot be established if large alkali-metal cations crowd the supercage of the zeolite.

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Zusammenfassung — Mittels TDP wurde die Wechselwirkung zwischen 1-Methylnaphthalin und den Alkalimetall- X und Y Zeolithen untersucht. Alle Spektren zeigen nur einen einzigen Peak, dessen zugehörige Temperatur sich mit Art und Menge des Alkalimetallkations und dem Si/Al-Verhältnis auf dem Faujasit ändert. Es wird eine Korrelation zwischen der Peaktemperatur und der Durchschnittsladung der Gitter-Sauerstoffatome der Zeolithe gezeigt. Auf der Basis der atomaren Ladungsverteilung im 1-Methylnaphthalin Molekül wird angenommen, daß Adsorption durch die Wechselwirkung zwischen dem Alkalimetallkation und dem Kohlenstoffatom der Methylgruppe initiiert wird. Gleichzeitig erfolgt eine Wechselwirkung zwischen den Wasserstoffatomen des aromatischen Ringes und den Gitter-Sauerstoffatomen der Zeolithe mit Ausnahme von X Proben, die einen hohen Anteil an großen Alkalimetallkationen aufweisen.