CORRELATIONS BETWEEN THE ACIDITY AND CATALYTIC PROPERTIES OF H,Na-MOR

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ABSTRACT

Acid centres formed by different degrees of decationization
have been characterized by the adsorption heat of ammonia and by I.R.
spectroscopy. We have established that H,Na-MOR shows a broad acid
strength distribution with distinct steps representing different acid
strengths. The active sites for m-xylene disproportionation and iso-
merization can be attributed to centres having adsorption heats for
ammonia above 150 kJ/mol, and 120-150 kJ/mol, resp. The disproportio-
nation centres are formed at higher degrees of decationization.

INTRODUCTION

Both isomerization and disproportionation of xylenes take place
on acid sites of zeolite catalysts. The ratio of the two transforma-
tions i.e. the selectivity depends on the reaction conditions, and on
the type and pretreatment of the catalyst [1, 2]. Therefore, different
mechanisms have been suggested for the monomolecular isomerization
and for the bimolecular disproportionation, which involve different
interactions between the acid catalyst and xylene. As a consequence
of this difference the selectivity can be expected to be influenced
by the strength and the number of acid sites. In addition, steric
factors may play an important role in the case of zeolites having pore
sizes commensurable with the molecular dimensions of xylenes [2].

The correlation between the catalytic properties and the degree
of decationization has been widely investigated for H,Na-Y,FAU [1].
It has been found that active sites of different activities were
formed at lower and at higher degrees of decationization [3, 4]. Sim-
ilar conclusions have been drawn for H,Na-MOR [5-7] but without any
detailed correlation with the acidity.

As it is well known acid sites can be studied conveniently by
I.R. spectroscopy [8]. The method provides with very important infor-
mations on the nature of acid centres, but the quantitative evalua-
tion of the results in rather troublesome. The strength and the number
of acid sites can also be determined by titration, the conditions of
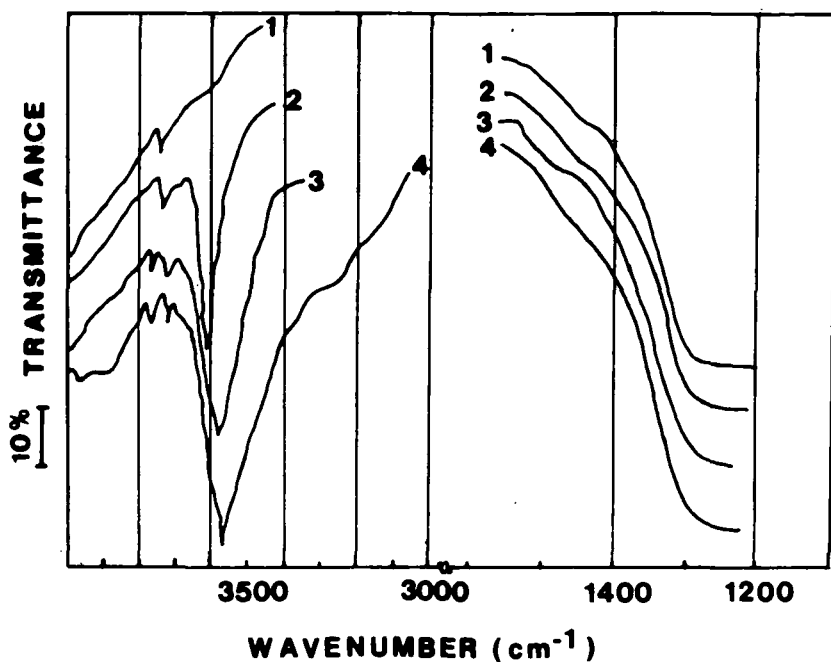which differ, however, essentially from those of catalytic reactions.

Fig. 1. Infrared spectra of NH_4,Na-MOR samples
after evacuation at 823 K for 5 hours. 1.: M-33;
2.: M-46; 3.: M-83; 4.: M-98.

The measurement of the adsorption heat of bases like ammonia seems more
promising [9, 10]. The microcalorimetric determination of differential
adsorption heat of small doses of ammonia affords to obtain the acid
strength distribution of the sites on the catalyst sample.

The aim of the present work was to determine the nature and the
acid strengths distribution of active sites in H,Na-MOR, and to cor-
relate them with the catalytic activities for xylene isomerization and
disproportionation.

EXPERIMENTAL

Preparation of catalysts

H,Na-MOR samples were prepared from Na-MOR (Zeolon 100, Norton
Co., USA) by ion-exchange for ammonium to different degrees in the
usual way. Samples of 33, 46, 83 and 98 per cent degree of ion-exchange
were produced (M-33, M-46, M-83, M-98). Thereafter they were pelletized
without binder. Activation was carried out in the reactor at 823 K for
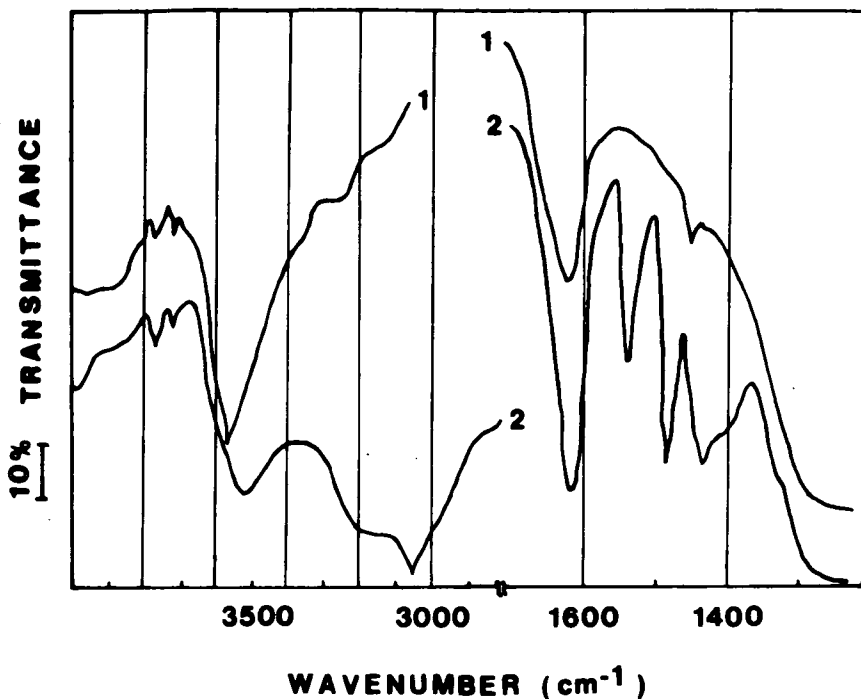
Fig. 2. Infrared spectra of M-98 sample.
1.: after pretreatment at 773 K for 5 hours;
2.: after pyridin adsorbed on the sample at
room temperature, at a pressure of 2.66 kPa.

8 hours in a flow of hydrogen.

Catalytic measurements

Transformations of m-xylene were determined in an integral flow reactor at 573 K, at space velocities between 2.5 and 13 $hour^{-1}$, at O.5 MPa hydrocarbon pressure and 1.5 MPa hydrogen pressure. Gaseous and liquid products were analyzed with a JEOL 810 gas chromatograph.

I.R. measurements

I.R. measurements were performed in a Perkin Elmer 577 spectro-photometer in the range of 1000-4000 cm^{-1}. The samples were pressed without binder in wafers of a thickness around 10 mg/cm^2.

Calorimetric investigations

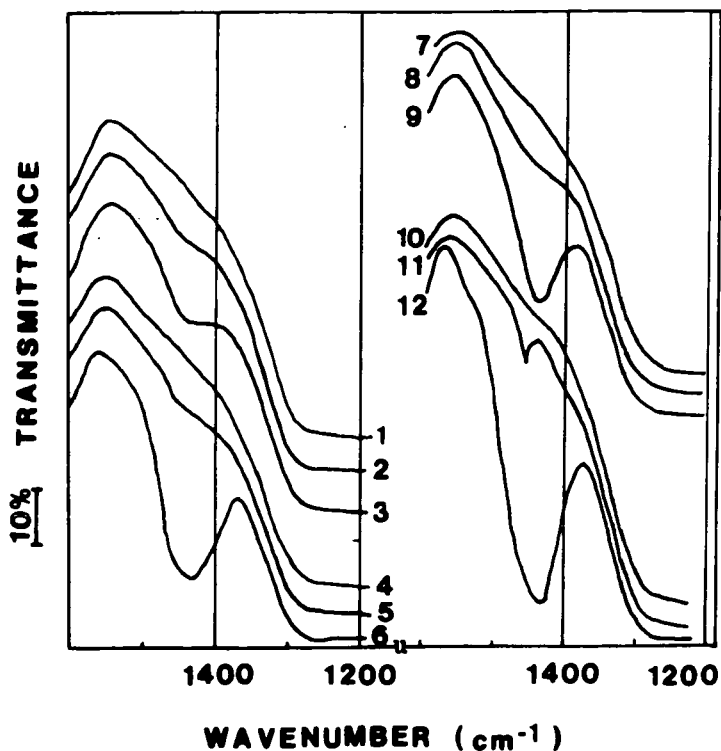Differential adsorption heat was measured in a Calvet calori-

Fig. 3. Infrared spectra of NH_4,Na-MOR samples
after evacuation at different temperatures for 5
hours, 1., 2., 3.: at 623, 573, 473 K for the
sample M-33; 4., 5., 6.: at 723, 673, 573 K for the
sample M-46; 7., 8., 9.: at 773, 723, 673 K for the
the sample M-83; 10, 11, 12.: at 823, 773, 673
for the sample M-98.

meter connected to a volumetric adsorption apparatus. Before adsorp-
tion samples were pretreated at 753 K for 40 hours at 10^{-3} Pa. Calori-
metric measurements were carried out by admitting small doses of ammonia
at 573 K. The details of the method are described in [11].

RESULTS AND DISCUSSION

I.R. spectra in Fig. 1 show the intensity changes of acidic OH
bands for samples of different degree of decationization. It is strik-
ing that practically no OH groups are detectable on the sample having
been exchanged for ammonium up to 33 per cent. Dehydroxylation should
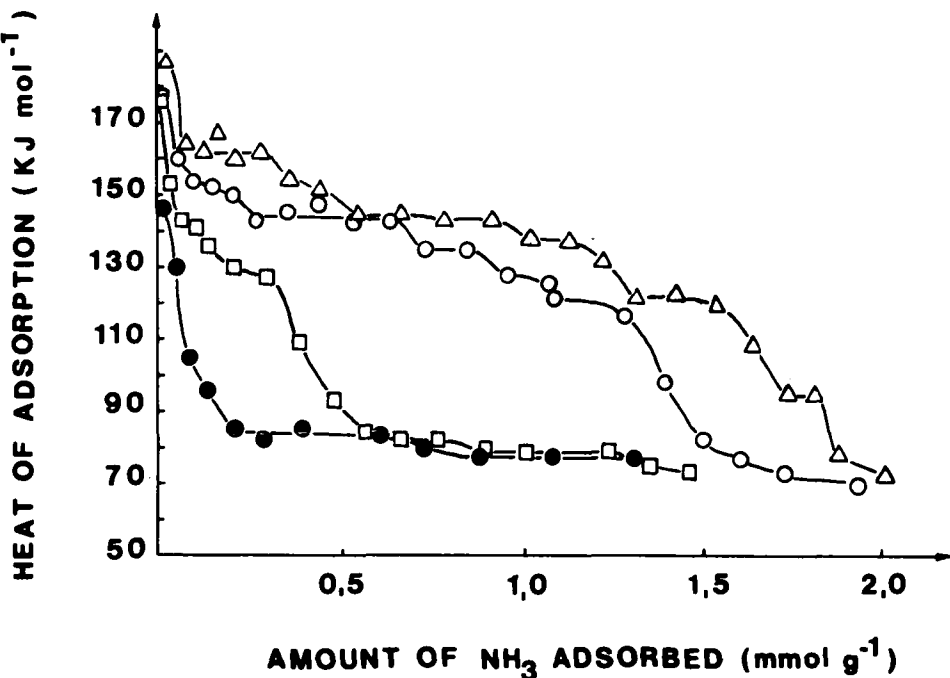
Fig. 4. Differential heat of adsorption as a
function of coverage. Adsorption of NH_3 was
carried out at 573 K, on M-98 ($\triangle$), on M-83 (o),
on M-46 ($\square$), on M-33 ($\bullet$).

accompany the total deammoniation being very pronounced in the case of
low degree of decationization. Dehydroxylation has been traced also for
the deeply exchanged sample M-98. Since dehydroxylation results in the
formation of Lewis acid sites [12] which can be easily detected by the
appearance of the typical absorption bands of pyridin bound to these
sites, the pyridin adsorption on sample M-98 pretreated at 773 K was
studied by I.R. spectroscopy (Fig. 2). Pyridin adsorption both on
Brönsted and on Lewis acid sites can be observed. The presence of Lewis
acid sites indicates a significant dehydroxylation Similar measurements
were carried out with sample M-33 after pretreatments at 623 and 823 K.
Even at 623 K dehydroxylation was detectable, and the ratio of Lewis
and Brönsted acid sites was as high 27.7 after a pretreatment at 823 K.
This ratio after a pretreatment at 823 K was 3.7 for sample M-98.

It is to be remarked that pyridin adsorption does not result in
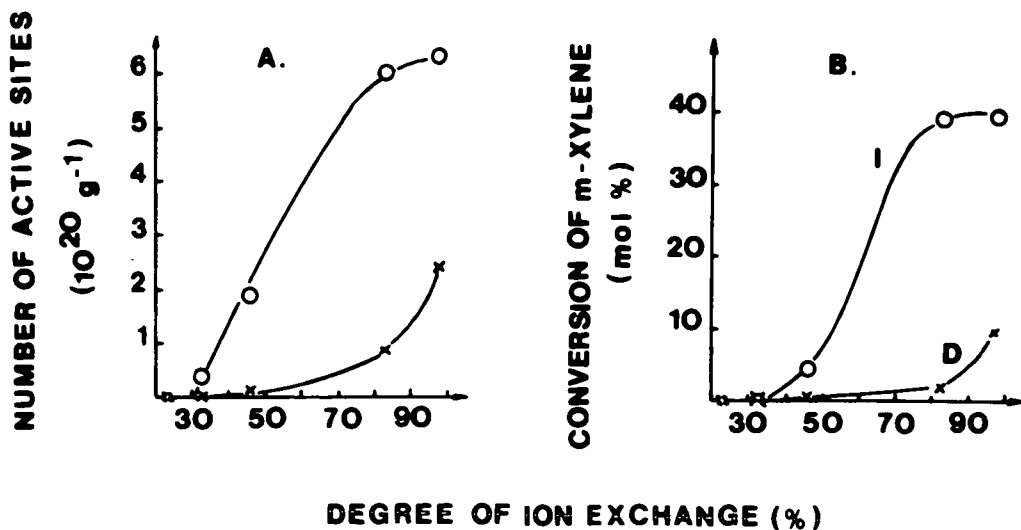the total disappearance of acidic OH vibration band (cf. spectra 1 and

DEGREE OF ION EXCHANGE (%)

Fig 5. A: number of active sites [$q_{diff}^{NH_3}$ = 120–150 kJ mol^{-1} (o), $q_{diff}^{NH_3}$ > 150 kJ mol^{-1} (x)], B: isomerization (o) and disproportionation (x) conversions as a function of degree of ion-exchange. Adsorption temperature 573 K, reaction temperature 573 K, initial pressures: 0.5 MPa m-xylene, 1.5 MPa hydrogen.
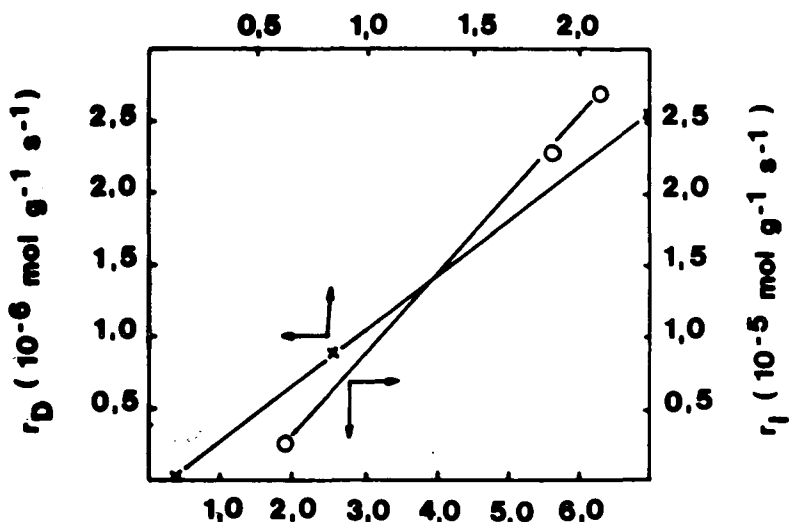
2 in Fig. 2 in the range of 2800-4000 cm^{-1}), which may indicate that a considerable fraction of Brönsted sites is not accessible for pyridin and neither it is for xylene.

The changes of deammoniation of samples M-33, -46, -83, -96 are illustrated in Fig. 3. The intensities of the bands in the range of ammonium deformation vibrations show that the higher the NH$_4$-ion exchange degree is the higher temperature is needed for the decomposition of the ammonium form under the given conditions. Acid sites of different strength can be concluded: increasing the degree of ion-exchange ammonium occupies stronger acidic sites.

A quantitative correlation between the strength and the number of acid sites can be established by the determination of differential adsorption heat of ammonia as a function of the adsorbed amount of ammonia for samples of different decationization degree (Fig. 4). In this way all the uncertainities of non-isothermic determination of isosteric adsorption heat can be avoided; i.e. on changing the temperature the

NUMBER OF ACTIVE SITES OF

$q^{NH_3} = 120 - 150 \ KJ \ mol^{-1} \ (10^{20} \ g^{-1})$

Fig. 6. Initial rates of isomerization (o) and disproportionation (x) as a function of the ion-exchange degree. Reaction conditions are the same as in Fig. 5B.

acid sites can be modified consequently the adsorption heat can change.

The curves in Fig. 4 show that the differential adsorption heat decreases with the coverage.

Being the adsorption heat of ammonia on Na-zeolites around 90 kJ/mol [11], the amount of ammonia bound with a higher energy has to be considered as chemisorbed on decationized sites.

A heterogeneous acid site distribution can be evidenced from the curves in Fig. 4. They are significantly different for the different decationized samples: the lower the degree of decationization by far less the number of stronger acid sites. Well-defined steps at the same heights are often observed on different curves reflecting the existence of distinctly different acid sites.

We tried to find correlation between the acidity and the activity for m-xylene isomerization and disproportionation. Isomerization and disproportionation conversions measured under identical conditions are plotted against the degree of ammonium ion-exchange (Fig. 5.B). As it has been mentioned the two transformation proceed on centres of different acid strength. We looked for acid sites of different strength having a number which shows a similar function of the ammonium ion-exchange as the activities.

The number of acid sites characterized by ammonia adsorption heats between 120 and 150 kJ/mol seems to change similarly with the ammonium ion-exchange (Fig. 5A) as the isomerization conversion, and the number of sites above 150 kJ/mol shows a similar curve (Fig. 5A) as the disproportionation conversion.

If the degree of ammonium ion-exchange is 33 %, no catalytic activities are observable, and the numbers of the corresponding active sites are practically zero.

More accurate and more reliable correlation can be established between the activities and acidities when the initial rates of isomerization and disproportionation are plotted against the number of the above active sites (Fig. 6).

The linear correlation substantiates the existence of distinct active sites responsible for the two transformations. The sections on the abscissa correspond either to the active sites accessible for ammonia but not for xylene (cf. pyridin adsorption in Fig. 2) or to the dehydroxylation which may be suppressed during the low temperature long time pretreatment for calorimetric measurements but takes place to some extent during the activation in the reactor.

These recognitions permit to prepare a decationized mordenite catalyst of high isomerization selectivity and of satisfactory activity: acid sites with more than 150 kJ/mol ammonia adsorption heat must not be formed. This can be attained by partial decationation and/or partial poisoning.

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