A DETAILED NMR STUDY TO THE POLARISATION OF NON-FRAMEWORK LA^{3}+ CATIONS WITH THE FRAMEWORK Y ZEOLITE: APPLICATION OF ^{29}SI, ^{27}AL MAS AND ^{27}AL MQ MAS NMR.

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ABSTRACT

In order to understand the effect of high-valent cations on the framework in Y zeolite a detailed ^{27}Al NMR and ^{29}Si NMR study to Y zeolite has been performed . ^{27}Al MQ MAS NMR has been applied to La exchanged Y zeolite in order to get a resolution of quadrupolar interactions . ^{29}Si NMR shows no dealumination has taken place after ion exchange of La(NO$_3$)$_3$ to different extends (up to 16.7 wt% La^{3+}). ^{27}Al MQ MAS NMR shows the 40 ppm peak visible in ^{27}Al NMR is a distorted tetrahedral coordinated Al in the framework, having a distorted electrical field around the Al atom caused by the three-valent cations. Linear correlations between the fraction of charge compensated by La^{3+} versus Na^{+} ions and the fraction of distorted Si and Al atoms in the zeolite framework are found. Now, it becomes clear how the multi-valent cations polarise the framework.

INTRODUCTION

Zeolites are a common used catalyst. However, the detailed relationship between local structure and catalytic activity remains in many cases unclear. The effect of steaming of zeolites, which often leads to enhanced activity, is poorly understood. Many models exist, such as increased acidity by polarisation of the acid sites by extra-framework species[1], or to the catalytic effect of Lewis acid sites on extraframework species[2]. In this respect, the co-ordination of aluminium. species in zeolite has been subject of much research. Frequently used techniques are ^{27}Al NMR and ^{29}Si NMR. ^{29}Si NMR allows for the determination of the Si/Al ratio of the framework of the zeolite, while taking respect of Löwensteins Rule. ^{27}Al NMR allows for the determination of the co-ordination of the aluminium species in the zeolite. Four, five and six-co-ordinated Al can be distinguished. However, since Al is a quadrupolar nucleus, peaks may be broadened as well as shifted, which makes interpretation of Al NMR spectra difficult[3].

Here we show a technique called Multiple Quantum (MQ) MAS, which gives resolution of the quadrupolar interactions by choosing a pulse scheme proposed by Frydman et al.[4]. The size of the quadrupolar coupling constant can be made and this value is used to fit the 1D ^{27}Al NMR spectra using real quadrupolar line-shapes. Using this technique the interaction of extra-framework ionic species with the framework can be investigated. Distortions of the framework become visible and it will be shown that the three-valent La ions polarise the framework.

EXPERIMENTAL

NaY was obtained (LZ-Y54) and ion exchanged with $La(NO_3)_3$ and calcined at 300°C for 3 hours. Using different $La(NO_3)_3$ concentrations and a second exchange for the highest concentration different La^{3+} concentrations are obtained. The notation La(Na)Yx is used, where x stands for weight % of La in the sample.

1D ^{27}Al MAS NMR and ^{29}Si MAS NMR data were taken on a Bruker 500AM with spinning speeds of 12.4 and 5 kHz respectively; MQ MAS was taken on a Bruker 300AM. Samples were overnight saturated over a 1 M NH_4Cl solution H_2O environment.

RESULTS

Figure 1 shows the ^{29}Si and ^{27}Al MAS NMR spectra of NaY and La(Na)Y16.7. The Na Y shows a characterestic pattern and a Si/Al ratio of 2.6 is calculated. The La(Na)Y 16.7 spectrum is deconvoluted using a NaY part and an additional LaY part, which is shifted about 5 ppm from the NaY part. The ratio of intensity for both parts is equal to the ratio of charge compensated by each of the two cations (calculated on basis of Na content). Thus a Si/Al ratio of 2.6 has been found.

The ^{27}Al NMR spectra show the typical tetrahedral framework peak at 60 ppm for NaY. In La(Na)Y16.7, in addition to this framework tetrahedral Al peak, a broad component at 40 ppm is visible, which must be assigned to framework aluminium, since all Al is in the framework.
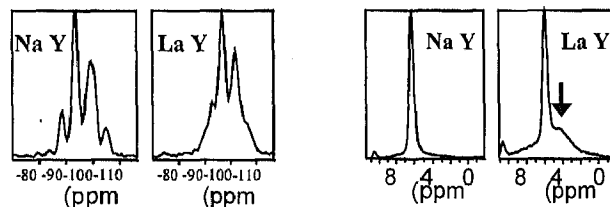

Fig1. ^{29}Si MAS NMR (left) and ^{27}Al MAS NMR (right) spectra of Na Y and La Y.

In Figure 2 the ^{29}Si MAS NMR (bottom) and ^{27}Al MAS NMR (top) of La(Na)Yx spectra are given. Each ^{29}Si MAS NMR can be fitted using a NaY part and a LaY part and in all cases a Si/Al ratio of 2.5/2.6 is found. The relative intensity of the LaY part of the spectra is an almost one to one function of the fraction of charge compensated by La^{3+} ions acting as charge balancing cations (calculated on the basis of each Na^+ ion balancing one negative charge, La^{3+}species balancing the rest). The ^{27}Al MAS NMR spectra show a clear increase in the intensity of the 40 ppm component upon increase of amount of La^{3+}.

The multiple quantum MAS ^{27}Al NMR is presented of La(Na)Y16.7 in Figure 3. This plot shows the 40 ppm peak for LaY to be caused by a quadrupolar broadened and shiftied tetrahedrally

co-ordinated Al. This plot makes an estimation of the quadrupolar coupling constants possible and these values are used to fit the quantitative 1D ^{27}Al MAS NMR spectra, being able to use quadrupolar line-shaped peaks. In this manner a linear relationship between the relative intensity of the 40 ppm peak and the percentage of charge compensated by the La^{3+} ions is found.
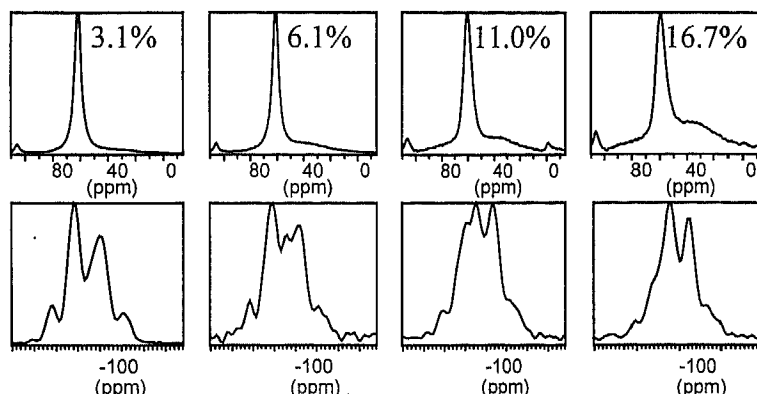

Fig 2. ^{29}Si MAS NMR (bottom) and ^{27}Al MAS NMR (top) spectra of La(Na)Yx. The weight percentages La are given.
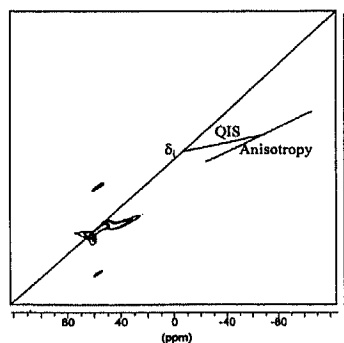

Fig 3. ^{27}Al MQMAS of LaY showing the origin of the 40 ppm peak. Projection on the x-axis reflect the 1D ^{27}Al NMR spectra.

DISCUSSION

The ^{29}Si NMR spectra indicate that for any La(Na)Yx all Al is in the framework after ion exchange of NaY with La(NO$_3$)$_3$. Thus all peaks observed in the ^{27}Al NMR must be framework Al. This is indicated as well by the absence of a 0 ppm peak which is in general attributed to non-framework octahedrally co-ordinated Al. The ^{29}Si NMR shows the effect of La^{3+} ions on the framework of the zeolite. The fraction of all Si atoms which is distorted by the La^{3+} ions is equal to

the fraction of charge compensated by the La^{3+} ions. This shows the overall effect the La^{3+} ions have on the framework.

The effect of La^{3+} ions on the Al atoms in the zeolite is shown by the ^{27}Al MQMAS NMR. The bending off the diagonal in the ^{27}Al MQMAS plot in the direction of the quadrupolar induced shift (QIS) as given by the arrows indicates the 40 ppm peak in LaY is a separate peak from the 60 ppm peak. The ^{27}Al MAS MQ NMR shows it can be attributed to a tetrahedrally co-ordinated Al species, experiencing a large electrical field gradient, which is caused by the La^{3+} ions present in the sodalite cages. The pretreatment of the samples will have caused the La^{3+} to migrate into the sodalite cages.
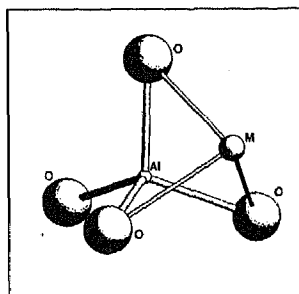

Fig 4. Schematic plot of tetrahedron in interaction with an AlO_4^{5-} tetrahedron of the framework.

Figure 4 shows a model of the interaction of the three-valent La ions with the AlO_4^{5-} tetrahedra in the framework. It has been proposed in the literature that increasing polarisation power (charge divided by radius) of cations cause a linear increase in distortion of the electrical field in AlO_4^{5-} tetrahedra in aluminosilicates'.

As one of the models presented in the introduction suggested that the La^{3+} ions polarise the framework, hence have a positive effect on the catalytic activity, it is now shown to what extend the ions polarise the framework. In the future more definite correlations between the polarisation of the framework and catalytic activity will be investigated.

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