

Hydrogen–Deuterium Exchange between Zeolite Y and 3-Methylpentane

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Zeolite Y undergoes hydrogen–deuterium exchange with 3-methylpentane at moderate temperatures (100 °C); the presence of non-framework aluminium species increases the reactivity of the zeolite.

Zeolites are acidic crystalline aluminosilicates that are widely used in the petroleum industry for cracking of high boiling hydrocarbons into gasoline and LPG.¹ Although carbocations are usually believed to be the intermediates in the cracking process,² there still exists a controversy as to the initial mode of carbocation formation in alkane cracking. Initial thermal cracking producing small amounts of alkenes which can be easily protonated, hydride abstraction by a Lewis acid site and direct protonation of the σ alkane bonds, passing through a five-coordinated carbocation, have been proposed as possible routes.^{2–4} On the other hand, hydrogen–deuterium exchange

between alkanes and superacids is usually believed to involve five-coordinated carbonium ions⁵ formed by protonation of the C–H bond of the alkane^{6,7} (Fig. 1). It also occurs under conditions under which cracking does not take place. In this work we report the hydrogen–deuterium exchange between deuteriated Y zeolites and 3-methylpentane (3MP) at 100 °C.

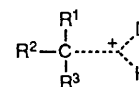


Fig. 1 Five-coordinated carbonium ion

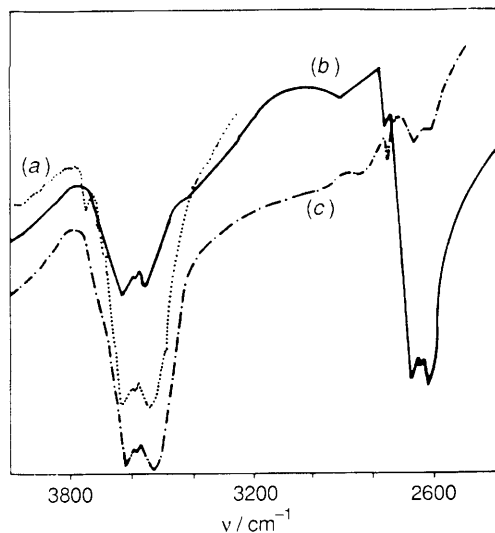


Fig. 2 IR spectrum of US(3): deep bed (600 °C for 30 min) and exchange with 1 mol dm⁻³ NH₄Cl: (a) 500 °C at 10⁻⁵ Torr; (b) D₂O, 200 °C for 1 h; (c) 3MP, 100 °C for 1 h

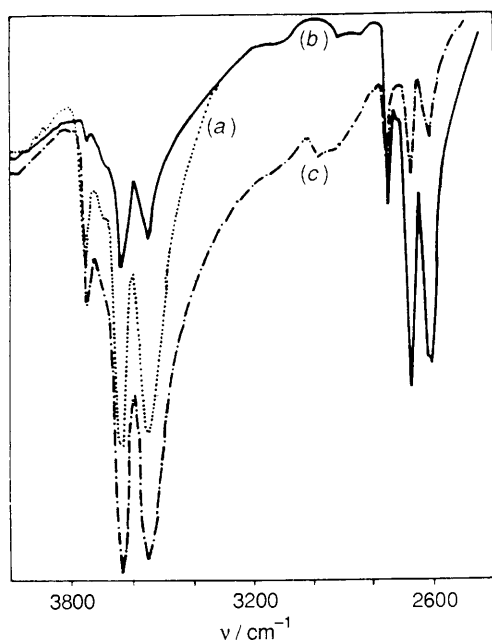


Fig. 3 IR spectrum of DY(3) 0.25 mol dm⁻³ Na₂EDTA (100 °C for 20 h)¹² and exchange with 1 mol dm⁻³ NH₄Cl: (a) 500 °C at 10⁻⁵ Torr; (b) D₂O 200 °C for 1 h; (c) 3MP, 100 °C for 1 h (EDTA = ethylenediaminetetraacetate)

The exchange reactions were followed by IR spectroscopy. A self-supported wafer of the zeolite was pre-treated at 500 °C and 10⁻⁵ Torr, deuteriated with D₂O at 200 °C for 1 h and exposed to 60 Torr of 3MP at 100 °C. After each treatment and before the IR measurements, the system was evacuated to 10⁻⁵ Torr. Under these conditions, there was no indication of cracking. All zeolites were prepared by dealumination of an initial NH₄Y with Si/Al = 2.4 and residual Na₂O of 4 wt%. Numbers in parentheses denote the framework Si/Al ratio measured by IR spectroscopy.⁸

Fig. 2 shows the IR spectrum of US(3). The OH region shows overlapping of the framework (3650 and 3550 cm⁻¹) and the non-framework (NFA) hydroxy absorptions (3690 and 3600 cm⁻¹), close to a small band at 3750 cm⁻¹ due to silanol groups. After deuteration and exposure to 3MP, these bands returned to their position in the non-deuteriated form,

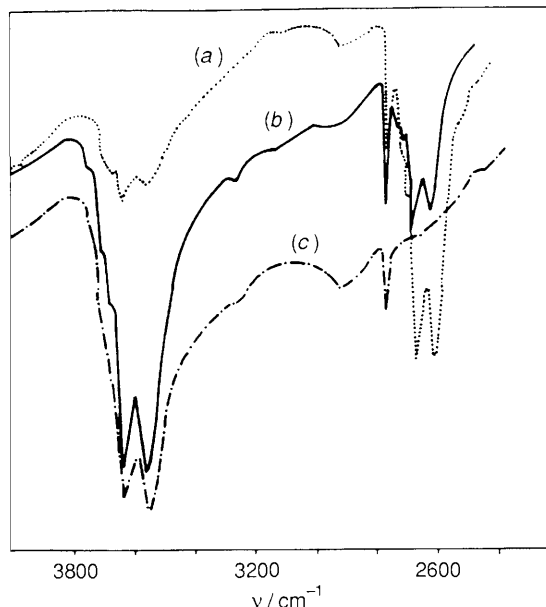


Fig. 4 IR spectrum of US(4.5): 100% steam (600 °C for 30 min) and exchange with 1 mol dm⁻³ NH₄Cl; kinetics of H-D exchange with 3MP at 100 °C: (a) 0 min; (b) 5 min; (c) 30 min

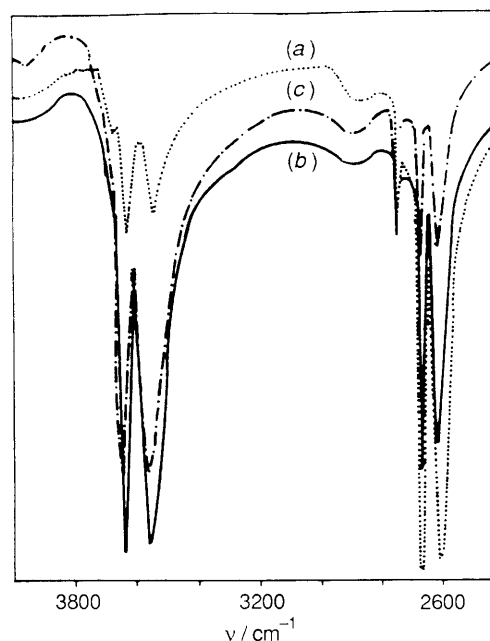


Fig. 5 IR spectrum of DY(4.3): 0.75 mol dm⁻³ (NH₄)₂SiF₆ (95 °C for 3 h)¹³ and exchange with 1 mol dm⁻³ NH₄Cl; kinetics of H-D exchange with 3MP at 100 °C: (a) 0 min; (b) 5 min; (c) 60 min

except the silanol band, which remained deuteriated. In Fig. 3, the IR spectrum of DY(3) shows the bands associated with framework hydroxy groups and silanol. Upon deuteration and exposure to 3MP, beside the silanol, a small proportion of the framework deuterioxy groups still remained unexchanged.

These results showed the similar reactivity of both (high and low frequency) framework hydroxy groups, and the reactivity of the NFA hydroxy groups. It is well known that the low-frequency framework and the NFA hydroxy groups are partially reactive and unreactive, respectively, towards pyridine.⁹ In the hydrogen-deuterium exchange with 3MP, perhaps a kind of hydrogen bridge interaction could be taking place, leading finally to the exchange of all the deuterioxy groups. To try to answer the questions of the similar reactivity

of the framework hydroxy groups in the exchange reaction and the effect of the NFA on zeolite reactivity, a kinetic study was carried out with two zeolites of similar Si/Al and sodium oxide content, differing only in the presence or absence of NFA.

Figs. 4 and 5 show the IR spectrum of US(4.5) and DY(4.3) respectively. US(4.5) with NFA showed a complete exchange in 30 min, while the DY(4.3) without NFA showed only a partial return even after 1 h. Only the silanol band remained unreacted. This suggests that NFA increases the zeolite acid strength. Similar results were also found for the cracking of n-hexane,^{10,11} where the presence of NFA increased the zeolite activity. The kinetic study showed that the framework hydroxy groups seem to have the same reactivity towards the exchange reactions. However, hydrogen bridge interactions cannot be ruled out, since rates for this process can be faster than the exchange rate, making the hydroxy groups appear exchanged. The same concept can be applied to the NFA hydroxy groups. An additional experiment with deuteriated γ alumina showed no exchange with 3MP, indicating low acid strength.

This study indicated that zeolites can protonate σ bonds of tertiary alkanes at 100 °C without cracking, probably through an intermediate or transition state having a five-coordinated carbonium ion, suggesting that this mechanism is reasonable in explaining the initial formation of carbocations in alkane cracking. The role of hydrogen bridge interactions on the reactivity of framework and non-framework hydroxy groups

and the incorporation of the deuterium in the 3MP are under investigation.

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