REACTIONS OF METHANOL OVER HIGHLY SILICEOUS ZEOLITES

By

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A family of novel zeolites with SiO_2/Al_2O_3 ratios between 45 and 120 has been designated Nu—1. Sorption studies indicate a port size of about 0.60 nm. HNu—1 resembles HZSM-5 in catalysing the conversion of methanol to aromatics, but the activity decays rapidly.

Introduction

In the 1960's and early 1970's there were high hopes that crystalline zeolites would yield fundamental insights into heterogeneous catalysis. We now know that this view was too optimistic, and that even zeolites have active sites with a spectrum of activities. However, in our view, catalysts based on radically different zeolite framework still offer the best chance of major advances in catalysis, especially in the petroleum field.

Recently new families of highly siliceous zeolites have been discovered e.g. ZSM—5 [1], and these offer the possibility of new catalytic processes.

In this work we compare methanol conversion over our novel zeolite Nu—1 with conversion over ZSM—5 and mordenite.

Experimental

Zeolite Nu—1

Zeolite Nu—1 has been synthesized from mixtures low in aluminium, and with tetramethyl ammonium (TMA) as major cation. It is readily distinguished from other highly siliceous zeolites by its very characteristic X ray diffraction data and infrared data. Detailed information on Nu—1 synthesis has been published only in patent form [2]. Table I gives typical X-ray data obtained on a Phillips diffractometer using copper K α radiation. Five different varieties of Nu—1 have been found as indicated by small but subtle variation in X ray data.

In as-made Nu—1 up to 2.5 moles of TMA can be occluded in the lattice, and this can only be removed by thermal/oxidative breakdown. Reproducible manufacture of Nu—1 catalysts is extremely difficult. From DTA studies it is clear that above 180 °C, even with low oxygen levels, runaway burn off can occur. Large exotherms

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Table I

Zeolite Nu—1 *in hydrogen form*

d (A)	100 I/I0	d (A)	100 I/I0	d (A)	100 I/I0
8.87	18	4.30	51	3.81	22
8.28	69	4.08	37	3.687	16
6.53	43	4.03	100	3.508	29
6.19	75	3.965	73	3.256	27
4.45	52	3.845	74	2.858	15

have been observed and local temperatures as high as 750 °C have been recorded. Significant lattice damage can occur at temperature exceeding 550 °C.

Unlike ZSM—5 and other highly siliceous zeolites Nu—1 does not show marked hydrophobic tendencies *i.e.* the ratio water sorption/*n*-hexane sorption is more typical of the hydrophilic zeolites such as A or X. The Nu—1 samples used in this work were prepared in a pyrex 25 litre lined autoclave under quiescent conditions at 180°C for 72 hours, from reaction mixtures of composition

$$12.6 \ Na_2O \ 5.4 \ (TMA)_2O \ Al_2O_3 \ 59.3 \ SiO_2 \ 3600 \ H_2O$$

After filtration, washing and drying for 17 hours at 120 °C the as-made Nu—1 had a composition

$$0.73 \ Na_2O \ 2.1 \ (TMA)_2O \ Al_2O_3 \ 50 \ SiO_2 \ 10.4 \ H_2O$$
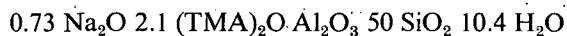
Nu—1 catalyst preparation

The Nu—1 was exchanged twice with 2 mls of 5% w HCl per g. After filtering, washing and drying at 120 °C the product was calcined in a stepwise manner from 150→450 °C (in air previously saturated at 25 °C with water). After 1 hour at each temperature a 50° step was taken. At 450 °C the temperature was held for 17 hours and then taken slowly up to 550 °C which was held for 3 hours. The product was

$$0.01 \ Na_2O \ Al_2O_3 \ 53 \ SiO_2$$

and contained 0.3% w carbon and <0.05% w nitrogen.

Sorption studies on Nu—1

In order to obtain reproducible sorption results it was necessary to thoroughly "clean up" the Nu—1. This was achieved by calcining in ammonia at 450 °C for 24 hours to break the TMA, mainly to carbonaceous residues, which could be burnt off fairly readily at 450 °C in air over a 24 hour period. The product contained <0.1% carbon.

Sorption data, obtained on McBain silica spring balances, is presented as kinetic curves in Figs. 1 and 2. All experiments were carried out at 25 °C and $P/p_0 \simeq 0.5$.
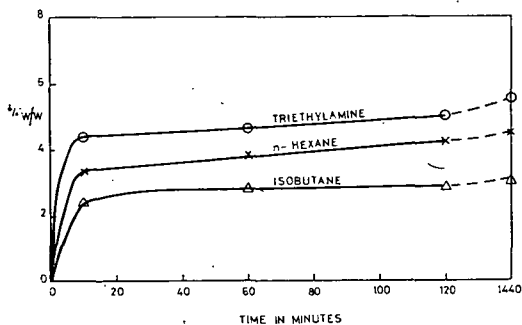
Fig. 1. Sorption rates for triethylamine,
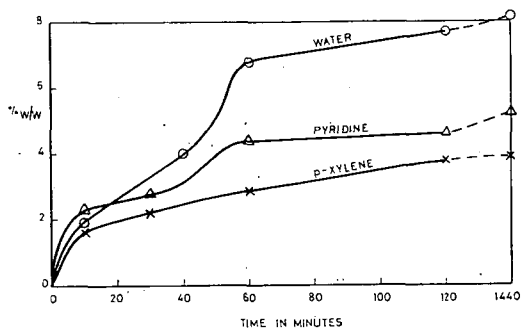*n*-hexane and isobutane at $P/p_0 = 0.5$, 25 °C

Fig. 2. Sorption rates for water,
pyridine and *p*-xylene at $P/p_0 = 0.5$, 25 °C

Catalytic reactions

A conventional pulse microreactor system was used to obtain the initial catalytic activity of Nu—1 in methanol conversion to hydrocarbon products. 1 or 2 μl injections of methanol were vapourised in a nitrogen stream, passed over 0.3—0.4 g catalyst pellets and the reaction products analysed on a GC column (3 m of 15% OV 101 silicone on Chromosorb, programmed for 60°—360 °C). A flow reactor (10 ml catalyst bed) with off-line analysis was used to find steady-state catalytic activity. On-line activation/regeneration of catalysts was possible in both units (typically 18 hours at 450 °C under fast air flow).

Several different samples of HNu—1 were tested in the pulse microreactor at 375° and 450 °C. Differences in activity for the conversion of methanol to hydrocarbons were found, but these could not be correlated with variations in either preparative method or physical properties (*e.g.* crystallite size, X-ray diffraction pattern) of the catalyst. Nevertheless the yields of aromatics were consistent over a range of conversions, and a similar product distribution was obtained from dimethyl ether feed. Aromatic product distribution for two samples of HNu—1 are shown in Table II. Very fast decay of hydrocarbonforming activity was found: the injection of 20 μl

Table II

Aromatic product distribution (% wt)

Microreactor unit	Pulse, 450 °C			Flow, 371 °C [4]
zeolite catalyst	$-$HNu$-$1 A*	HNu$-$1 ·B*	HZSM$-$5	HZSM$-$5
Benzene	1	8	14	4.1
Toluene	17	12	33	25.6
Ethylbenzene	33	20	24	34.7
m-, p-Xylene, o-Xylene	10	5	8	9.0
C_9	21	23	9	19.1
C_{10}	14	26	6	7.0
C_{11}^+	4	6	6	0.4

* Activity of sample A about 10 x activity of Sample B.

CH_3OH (10x initial pulse) was found to decrease total aromatics (from a subsequent 2 µl CH_3OH) by about 60% and after ·60 µl CH_3OH aromatics formation was negligible. Calcination in air restored the original activity.

A sample of the same batch B of HNu—1 was used with CH_3OH feed in the flow reactor at 375° and 450 °C, LHSV 1—2 hr^{-1}. Dimethyl ether was the only gaseous product and no hydrocarbons were found.

Discussion

Sorption

The sorption results suggest that Nu—1 has ports close to 6A because molecules such as xylenes enter somewhat sluggishly and large molecules *e.g.* symmetrical trimethylbenzene are only adsorbed on the external surface. Sorption in zeolites always occurs by activated surface diffusion because the inter-crystalline channels are so narrow that real gas phases cannot exist. The results for sorption of isobutane, *n*-hexane and triethylamine (Fig. 1) are typical of sorption on zeolites where the molecules are significantly smaller than the zeolite ports. However triethylamine has a Lennard-Jones minimum kinetic diameter of 7.8 A [2]. The rate curves for water, p-xylene and benzene suggest there is a significant barrier to entry of the Nu—1 lattice and that after a significant time delay activated diffusion occurs in an auto-catalytic manner. The results for water $\sigma = 2.8$ A are puzzling, but may be related to the high silica content of Nu—1, the barrier here may be hydrophobic siloxane rings which perhaps eventually hydrate and then allow access of further water. In the truly hydrophobic zeolites *e.g.* ZSM—5 this does not occur, water only has access to a limited portion of the voidage which is available to hydrocarbons.

Catalysis

The formation of aromatics from methanol over Nu—1 is evidence that some catalytic sites in Nu—1 are strongly acidic. Both the carbon-carbon bond formation and the hydrogen transfer reactions necessary to give aromatics from the intermediate products of methanol conversion are probably carbonium-ion reactions. The distri-

bution of aromatics (Table II) is broadly similar to that found with HZSM—5 catalysts [4, 5] with toluene and xylene as main products, but little benzene is found with NHu—1. The product end-point at about C_{10} aromatics, as with HZSM—5, is probably due to steric constraints. The small proportion of C_9, C_{10} aromatics arise from their low diffusivity in NHu—1 at 375°—450 °C. No measurable sorption of these compounds was found at 25 °C.

The rapid decay of hydrocarbon formation over Nu—1 is in contrast to the stability of ZSM—5 [4], but shows similarities to mordenite in hydrocarbon formation at 400 °C [6] and in CH_3OCH_3 formation at 155°—240 °C [7]. Complete deactivation of Nu—1 needed about 5 molecules CH_3OH/Al atom. Even if no volatile products were formed there was insufficient polymeric material to block all acid sites. Deactivation by pore-mouth blocking, as probably occurs in mordenite [6, 7], and catalysis by only a small fraction of acid sites are possible explanations. The continued formation of dimethyl ether probably occurs on unpoisoned weak acid sites, including any on the crystal exterior.

After the initial formation of C_2H_4 from CH_3OH over strongly acidic zeolites, conventional carbonium ion reactions can explain, qualitatively at least, the formation of aromatic or non-aromatic [6] hydrocarbons. Strong acidity of the high-silica zeolites, mordenite, ZSM—5 and Nu—1, is needed for a fast initial step, which therefore involves cationic intermediates. However, neither CH_3^+ nor oxonium ions ($CH_3OH_2^+$, etc) are plausible intermediates, so the mechanism remains obscure.

References

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