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Propane Conversion on Dry-air-calcined HZSM-5 Zeolite

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Propane conversion has been studied at high and low partial pressures on HZSM-5 based catalysts which had been dry-air calcined at temperatures between 773 and 1193 K. At a low partial pressure (36.5 Pa), where products at 808 K were restricted to methane, ethene and propene, attention is directed towards the relative contributions from cracking and dehydrogenation in the initial activation of propane. An excess of ethene over methane and differences in the activation energies for their formation suggest that cracking of both C_3 and C_6 carbenium ions contribute to ethene production. Both unbound and silica-bound HZSM-5 catalysts were used in these low-partial-pressure studies, where the rate of propane conversion expressed per g of zeolite was 25 ± 4% less for bound catalysts calcined at the same temperature. At a high partial pressure (101 kPa), where methane, ethane and various aromatics were the predominant products, activity measurements were restricted to silica-bound HZSM-5 at 808 K. In both pressure regimes the concentration of Al atoms occupying tetrahedral positions within the framework structure is fundamental in determining activity patterns.

The initial activation and subsequent aromatisation of short-chain alkanes is of both academic and industrial interest, in that the reactions on a single catalyst form the basis of the BP/UOP[1] and Mobil[2] processes for the production of aromatics. The catalysts used are based on acidic HZSM-5 zeolite, into which Ga or Zn are frequently introduced by various methods.[3] Research shows that HZSM-5/Ga catalysts are bifunctional, where cracking, oligomerisation and cyclisation are associated with the acidic function, whilst dehydrogenation of alkanes and naphthene intermediates is associated with the gallium moiety.[4–10] The nature of the active gallium remains under debate, but species ranging from the structural charge balancing Ga^{3+}, Ga^+ and GaO^+ ions to neutral polynuclear oxides, in the zeolitic pores or on the crystallite surfaces, have been considered.[3,9]

With non-loaded HZSM-5 zeolites, which are usually lower in both activity for alkane conversion and specificity for aromatic formation, the position is even less clear. Enhanced activity for hexane cracking following steaming indicates that structural dealumination generates sites of higher specific activity.[11] A 'volcano'-shaped plot of the activity of HZSM-5 for propane conversion at 723 K *vs.* calcination temperature[4,12] suggests that the reaction requires superactive sites involving both structural and extrastructural Al atoms. Alternatively, structural Al may provide both Brønsted and Lewis acid centres, whereas extrastructural Al is associated with dehydrogenation centres. A maximum in the activity of HZSM-5 for propane conversion at 808 K was also observed after dry-air calcination had reduced the structural Al content from an initial value of 5.5 to 3.1 Al atoms per unit cell.[13] This paper reports an investigation of propane conversion at high and low partial pressures on HZSM-5 based catalysts which had been dry-air calcined at temperatures between 773 and 1193 K. To investigate primary products from propane activation, experiments were made at low partial pressures to minimise the subsequent reactions leading to aromatic compounds. However, to generate secondary products, such as aromatics, it was necessary to use a higher catalyst mass and a propane pressure of 1 atm.

Experimental

The preparation of both unbound and silica-bound NH_4ZSM-5 zeolites and their subsequent dry-air calcination at different temperatures to give a range of HZSM-5 catalysts has been described in a previous publication.[13] The starting material for all catalysts was a fully ammonium ion-exchanged NH_4ZSM-5 zeolite; conventional analysis gave a unit cell composition of $(NH_4)_{5.8}(AlO_2)_{5.8}(SiO_2)_{90.2} \cdot 18H_2O$, whilst plasma-source mass spectrometry showed the sodium content to be below the ppm level. The catalysts were thoroughly characterised by mid-IR spectroscopy, ^{27}Al MAS NMR spectroscopy and temperature-programmed desorption (TPD) spectra of NH_3; details of these catalysts relevant to the present investigation are given in ref. 13, Table 1. Unbound catalysts, dry-air calcined in the reactor prior to catalytic measurements, are designated HZSM-5/*x*, where *x* denotes the calcination temperature in K. Silica bound catalysts, dry-air calcined in 6 g batches in a separate calciner vessel, are designated HZSM-5/B/*x*.

All measurements of propane conversion at low partial pressure were made in a continuous-flow microreactor system where the total pressure was atmospheric (*ca.* 10^5 Pa). The catalyst mass used was 100 mg and the reactant mixture was a 30 cm^3 min^{-1} flow of propane (36.5 Pa) in helium diluent, corresponding to a propane feed rate of 4.52×10^{15} molecules s^{-1}. Samples of the product stream, taken at 20 min intervals over the first hour and then hourly, were automatically injected into an on-line Pye-Unicam GCD gas chromatograph coupled to a Pye-Unicam PU4811 computing integrator. The reactant–product mixture was separated on a 2.1 m column of Poropak Q at 313 K. Measurements of the catalytic conversion of pure propane at atmospheric pressure were made with silica-bound catalysts in a continuous-flow system at the BP Research Centre, Sunbury. This system was of a greater capacity than that used for measurements at low pressure, in that an accurately weighed catalyst charge of 6 g was used. Catalysts were activated at the reaction temperature of 808 K for 1 h in a 60 cm^3 min^{-1} flow of pure, dry N_2, before a propane reactant flow of 50 cm^3 min^{-1}, corresponding to 2.09×10^{19} molecules s^{-1}, was passed through the catalyst bed. This reactant flow was accurately maintained by a mass flow controller, whilst gas and liquid products were analysed by gas chromatography.

Following catalytic measurement at both low and high propane pressure, the catalysts were purged of volatile material by flowing helium before cooling to room temperature in the same gas. The carbon content of the spent catalysts were determined using a Perkin-Elmer 240B elemental analyser.

Results and Discussion

Propane Conversion at Low Pressure

To investigate primary product formation from propane it was necessary to minimise the subsequent reactions of oligomerisation, cyclisation and aromatisation. This was achieved using a low partial pressure of propane (36.5 Pa) and a low catalyst mass (100 mg), such that a reactant mixture flow of 30 $cm^3 min^{-1}$ gave a residence time for propane within the catalyst bed of 0.33 s. At the chosen reaction temperature of 808 K the major products were methane, ethene and propene, where r_M, r_E and r_{PE} are their respective rates of formation per g of zeolite, expressed in molecules $g^{-1} s^{-1}$. The only other detectable product was a trace of ethane. Rates of formation of the major products were determined for all HZSM-5 catalysts as a function of time on stream for experiments of 18 h duration. Product formation can be expressed in terms of the equivalent conversion of propane r_{PA} by the relationship $r_{PA} = (r_M + 2r_E + 3r_{PE})/3$, although this must be an approximation since it fails to include ethane and coke formation.

Plots of r_{PA} *vs.* time-on-stream for HZSM-5/833 and HZSM-5/1013 are shown in Fig. 1; the linear fall in activity with time is characteristic of all unbound and silica-bound HZSM-5 catalysts studied, which show average activity falls of 25 ± 6% and 23 ± 7%, respectively, over 18 h on stream. Such activity falls are associated with poisoning by progressive coke formation. Assuming the coke to be involatile, the carbon content of spent HZSM-5/833 and HZSM-5/1013 corresponds to 2.63% and 3.08% of the total 4.86×10^{-4} mol of propane passed in 18 h. Clearly, appreciable amounts of reactant propane in these low-pressure experiments are converted to coke without the appearance of C_4–C_6 aliphatics or volatile aromatics in the gas phase.

The activity of unbound HZSM-5 catalysts as a function of the temperature of dry-air calcination after 1, 4 and 16 h on stream is plotted in Fig. 2. These 'volcano'-shaped plots show the calcination at 1013–1033 K yields the most active catalysts and confirm the general fall in activity with time on stream. Values for r_{PA} at 20 min on stream, given in our earlier publication,[13] yield a similar volcano-shaped peak, but at a slightly higher activity level. Ono and co-workers[4,12] observed a similar peak in activity for propane conversion on HZSM-5, although the maximum followed dry-air calcination at the lower temperature of 853 K. For pentane, hexane and heptane cracking and *o*-xylene isomerisation the authors found evidence for two activity maxima following pretreatment at 673 and 853 K.[12] With ethylbenzene conversion, on the same catalysts used in the present study, there was an activity maximum following calcination at 1028 K and a shoulder following calcination at *ca.* 880 K.[13] Fig. 2 shows some evidence for a shoulder at *ca.* 900 K, but it is less pronounced than with ethylbenzene conversion. Differences between the observations of Ono and co-workers[4,12] and ourselves probably arise from differences in the initial Si/Al ratio of the zeolites and the 'dryness' of the calcination gas.

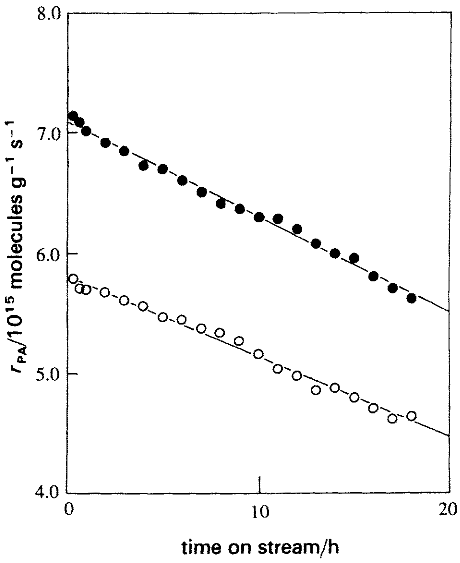

Fig. 1 Activity of HZSM-5 catalysts for propane conversion at low pressure *vs.* time on stream at 808 K: ○, HZSM-5/833; ●, HZSM-5/1013

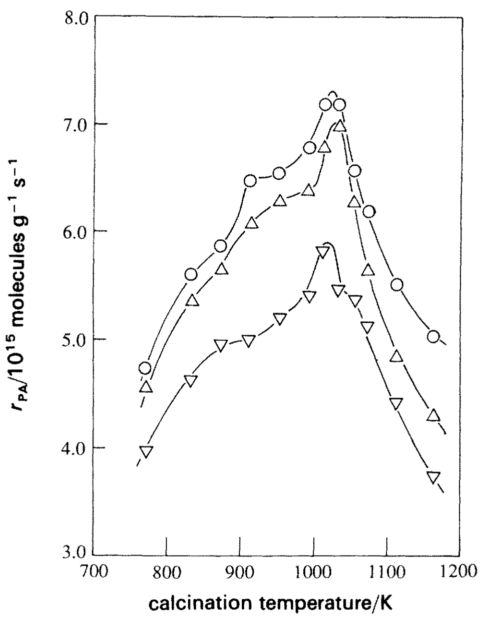

Fig. 2 Activity of unbound HZSM-5 catalysts for propane conversion at 808 K after ○, 1; △, 4 and ▽, 16 h on stream *vs.* temperature of dry-air calcination

It is instructive to consider the rates of formation of the separate reaction products; plots of r_M, r_E and r_{PE} after 1 h on stream are given for all unbound and bound catalysts as a function of calcination temperature in Fig. 3. Clearly r_{PE} is considerably less sensitive to calcination temperature and silica binding than either r_M or r_E, where r_E exceeds r_M for all HZSM-5 catalysts. Fig. 3 also emphasises that the change in catalyst morphology from powder to particle form, brought about by silica binding, is accompanied by a diminution in activity; the average reduction in r_{PA} after 1 h on stream is 25 ± 4% for pairs of catalysts calcined at identical temperatures. The reduction in activity is also reflected in a fall in the carbon content of the spent catalysts; from the data plotted in Fig. 4 the average carbon content of bound catalysts is 33 ± 11% less than that of the corresponding unbound catalyst.

Initial activation of propane by protonation of a C—C or C—H bond by a Brønsted acid site forms a carbonium ion, which may break down either by C—C cleavage to methane and ethene or dehydrogenate to propene; these steps are shown in Fig. 5. The figure also shows how, in the presence of a Lewis acid site created by structural dealumination during calcination, hydride abstraction followed by proton abstraction can lead to propene formation. Assuming the absence of Lewis acidity in the uncalcined catalyst, supported by the absence of extrastructural Al contributing to ^{27}Al

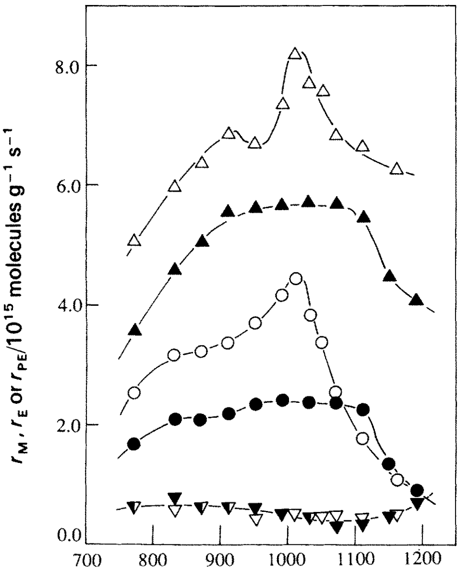

Fig. 3 Activity of unbound and silica-bound HZSM-5 catalysts for methane, ethene and propene formation at 808 K after 1 h on stream *vs.* temperature of dry-air calcination. Unbound catalysts: ○, r_M; △, r_E; ▽, r_{PE}. Bound catalysts: ●, r_M; ▲, r_E; ▼, r_{PE}.

MAS NMR spectra,[13] the ratio of dehydrogenation to cracking r_D/r_C, should be given by the ratio r_{PE}/r_M as long as r_E/r_M equals unity, *i.e.* only primary reaction products are being observed. Since r_E exceeds r_M for all catalysts studied, some assumptions have to be made before r_D/r_C can be estimated. The bimolecular dimerisation of two C_3 species to a C_6 carbenium ion, with subsequent cracking to yield three ethane molecules, is taken to be the source of the 'excess' ethene. Propene readily dimerises on HZSM-5, but at room temperature gives a methylpentene carbenium ion;[14] cracking yields ethene and an isobutene carbenium ion which would subsequently yield methane and propene. Clearly, this equal production of methane, ethene and propene cannot account for the ethene excess observed here at 808 K. Therefore every three excess ethene molecules have originated from two propene molecules; values of r_D/r_C calculated on this basis are plotted *vs.* calcination temperature in Fig. 6 and 7. Since the calculation ignores coke formation, in which the C_6 carbenium ion is also an intermediate, the r_D/r_C ratios are not maximum possible values. Nevertheless, Fig. 6 and 7 show that both unbound and bound HZSM-5 catalysts exhibit a region where r_D/r_C is near unity and insensitive to calcination temperature, although the ratio falls with time on stream. Following calcination at higher temperatures, where pronounced structural dealumination was observed,[13] both classes of catalyst show a rapid rise in r_D/r_C. The predominance of dehydrogenation in this latter region arises from the loss of Brønsted acid sites associated with cracking and the concomitant generation of extrastructural Lewis acid sites which may facilitate dehydrogenation by hydride ion extraction.

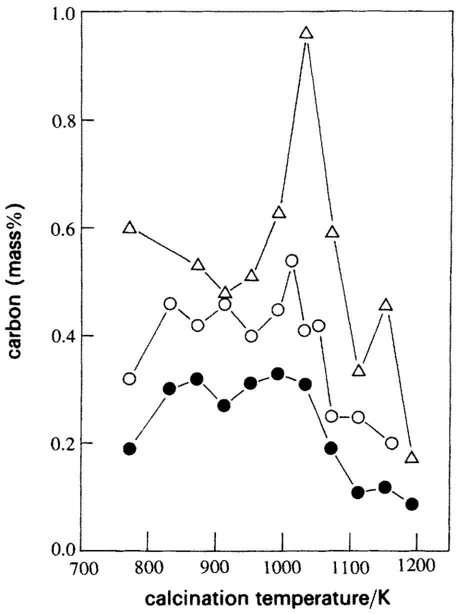

Fig. 4 Carbon content of spent catalysts: ○, HZSM-5 catalysts after 18 h at low pressure; ●, HZSM-5/B catalysts after 18 h at low pressure; △, HZSM-5/B after 6 h at high pressure

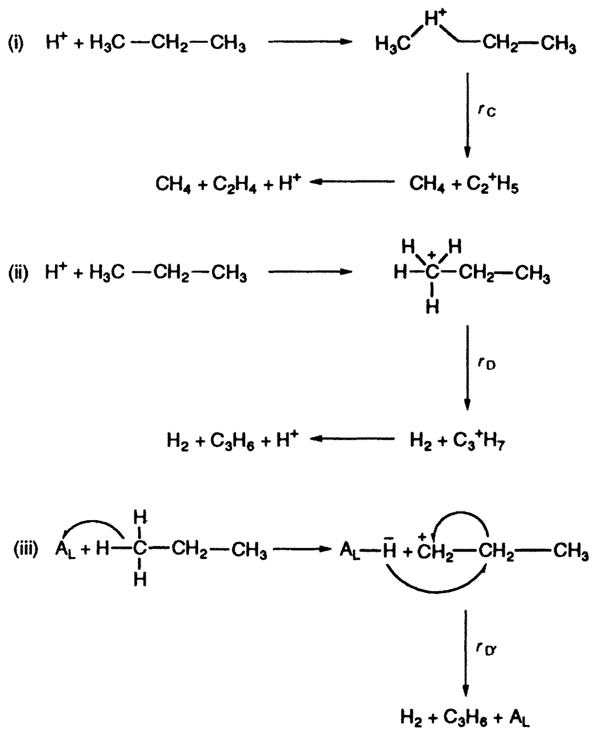

Fig. 5 Primary product formation in the acid catalysed activation of propane: (i) protolysis of C—C bond; (ii) protolysis of C—H bond; (iii) hydride ion abstraction

The effect of temperature on the rates of product formation was determined with HZSM-5/873 and HZSM-5/1013 at 788, 798, 808, 818 and 828 K. Values of r_M and r_E at 2, 8 and 16 h on stream gave good quality Arrhenius plots and the activation energies obtained are given in Table 1. Both HZSM-5/

Table 1 Activation energies for methane and ethene formation on HZSM-5 catalysts as a function of time on stream

catalyst	time on stream /h	$E_{methane}$ /kJ mol^{-1}	E_{ethene} /kJ mol^{-1}
HZSM-5/873	2	126	81
	8	136	83
	16	132	84
HZSM-5/1013	2	125	84
	8	122	85
	16	118	92

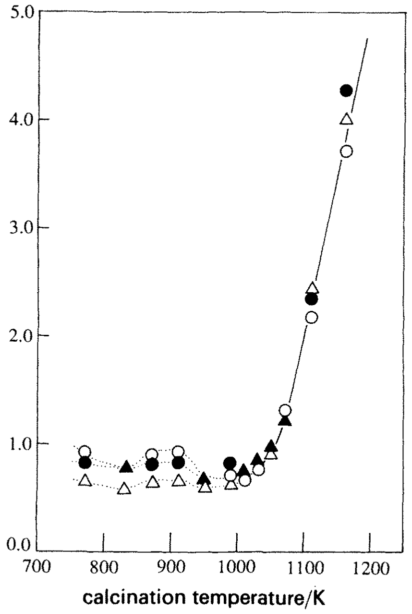

Fig. 6 r_D/r_C *vs.* calcination temperature for unbound HZSM-5 at ○, 1; ●, 4 and △, 18 h on stream. ▲, Graphically indistinguishable values obtained for different times on stream.

873 and HZSM-5/1013 showed a linear fall in activity over 18 h on stream, which corresponded to 25 ± 3% of the initial activity, irrespective of the reaction temperature. It follows that this decrease in activity would affect pre-exponential factors, but not activation energies, obtained from Arrhenius plots. Within the limits of error, the activation energy for ethene formation is the same for the two catalysts, whereas that for methane is *ca.* 10 kJ mol^{-1} lower over the more active catalyst. This lowering of the activation energy for methane may reflect the greater strength of Brønsted acid sites in more strongly dealuminated catalyst. Scatter in low values for r_{PE} precluded calculation of the activation energy for propene formation. If all methane and ethene were produced by cracking, sequence (i) in Fig. 5, then similar activation energies for their formation might be expected. An activation energy for ethene formation that is, on average, 42 ± 9 kJ mol^{-1} less than that for methane formation, supports the alternative route to excess ethene *via* dehydrogenation, dimerisation and cracking. Bandiera and Ben Taarit[15] concluded that r_D/r_C for propane was independent of acid strength, topology or temperature owing to the formation of the same carbonium ion in both pathways. However, we have shown that dehydrogenation can be partially decoupled from cracking by the introduction of Lewis acid sites, so that r_D/r_C is no longer independent of temperature.

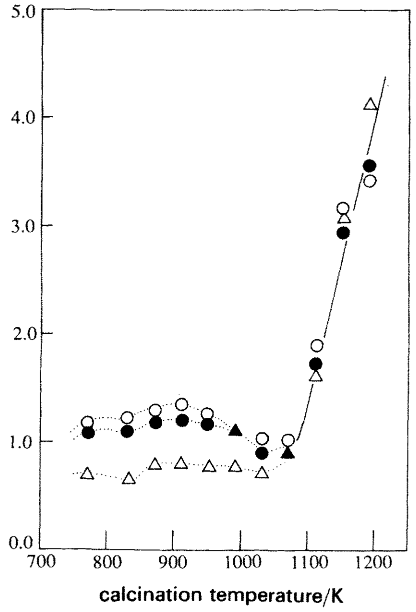

Fig. 7 r_D/r_C *vs.* calcination temperature for silica-bound HZSM-5 at ○, 1; ●, 4 and △, 18 h on stream. ▲, Graphically indistinguishable values obtained for different times on stream.

Propane Conversion At High Pressure

To investigate the formation of secondary products, such as aromatic compounds, from propane activation it was necessary to increase both the residence time in the catalyst bed and the propane pressure to atmospheric. A catalyst bed occupying 10 cm^3, consisting of 6.0 g of silica bound HZSM-5 zeolite, together with a propane flow of 50 $cm^3\ s^{-1}$ gave a residence time of 12 s, which is 36 times greater than that in the low-pressure experiments.

Catalytic experiments at 808 K were of 6 h duration, consisting of a 1 h equilibration period followed by three 1.5 h test periods at 1.0–2.5, 2.5–4.0 and 4.0–5.5 h on stream. The liquid products for each test period were collected and analysed, whilst the gaseous products were analysed at least three times in each test period. Table 2 presents the data, expressed in terms of mass%, obtained with HZSM-5/B/1033; although this was the most active catalyst the data are representative of all catalysts in that the activity is effectively independent of time on stream. From Table 2 it is clear that methane (25.0%), ethane (19.4%) and aromatics (26.7%) are the major products from propane conversion at atmospheric pressure. The formation of low-molecular-weight compounds with high H/C ratios, together with significant molecular hydrogen, results from the hydrogen balancing which accompanies the formation of aromatics with H/C ratios that are low with respect to the reactant propane. Fig. 8 presents plots of the yield of the major products, together with the extent of propane conversion, as a function of the catalyst calcination temperature. A volcano-shaped activity peak is obtained once more, both for propane conversion and for each major

Table 2 Product yields for propane conversion on HZSM-5/B/1033 as a function of time on stream at 808 K

	time on stream/h		
component	1.75	3.25	4.75
hydrogen	1.06	1.18	1.09
methane	24.58	25.10	25.24
ethene	3.19	3.02	3.14
ethane	19.76	18.68	19.67
propene	2.34	2.11	2.20
propane	21.06	20.91	20.62
butenes	0.61	0.56	0.58
butanes	1.13	0.94	1.01
higher aliphatics	0.00	0.00	0.00
benzene	7.94	8.97	8.11
methylbenzene	9.73	9.94	9.95
C_8 aromatics	4.54	4.74	4.74
C_9 aromatics	0.95	0.96	0.92
C_{10} aromatics	0.22	0.18	0.15
naphthalene	1.06	1.00	0.90
methylnaphthalene	1.30	1.21	1.10
dimethylnaphthalene	0.53	0.50	0.40

Yields expressed as mass%.

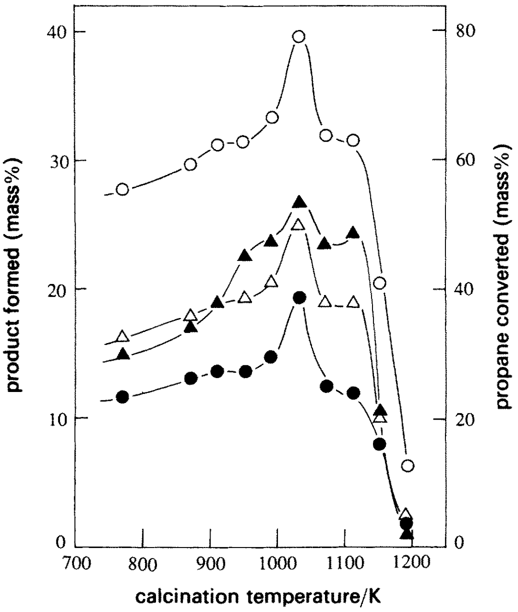

Fig. 8 Activity of silica-bound HZSM-5 catalysts for propane conversion at high pressure and 808 K *vs.* calcination temperature. ○, Propane converted; △, methane produced; ●, ethane produced; ▲, aromatics produced; all expressed in mass%.

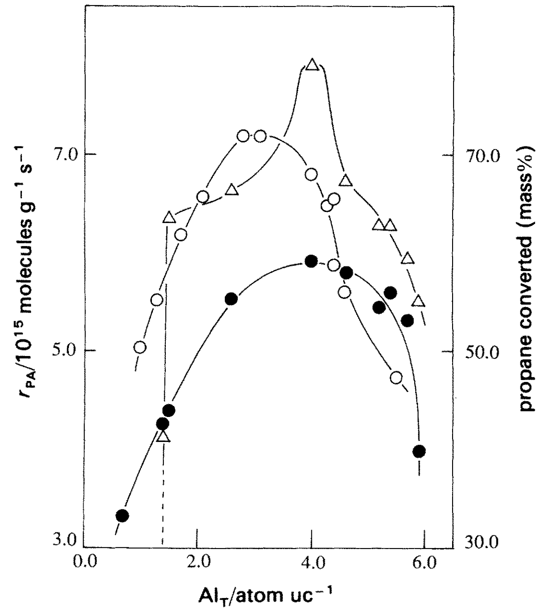

Fig. 9 Activity for propane activation at 808 K *vs.* tetrahedral aluminium content: ○, unbound HZSM-5 at low pressure; ●, bound HZSM-5/B at low pressure; △, bound HZSM-5/B at high pressure

product; HZSM-5/B/1033 is clearly the most active silica-bound catalyst, as it was for low-pressure propane conversion and ethylbenzene disproportionation.[13] The carbon content of the spent catalysts after 6 h on stream, given in Fig. 4, qualitatively parallels the activity pattern. For HZSM-5/B/1033 the carbon content corresponds to 0.21% of the total 0.748 moles of propane passed in 6 h, whilst for the least active catalyst, HZSM-5/B/1193, it corresponds to 0.038% of the propane passed. Thus although coking is more extensive over 6 h at high pressure than over 18 h at low pressure, the percentage of reactant propane lost to coke is considerably less.

Calcination Temperature Effects

The marked dependence of the activity of HZSM-5 zeolites for propane activation and aromatisation on the temperature of dry-air calcination is clearly seen in Fig. 2, 3 and 8. A maximum in activity at 808 K after calcination of 1013–1033 K applies at low pressures with both unbound and silica-bound catalysts and at high pressures with silica-bound catalysts. There is little doubt that the observations result from a variation in the concentration of active sites generated during calcination; a view supported by the similarity in activation energies found for product formation on HZSM-5/873 and HZSM-5/1013.

From an investigation of the effects of calcination temperature on the physico-chemical properties of the same Na free HZSM-5 zeolites used in the present study,[13] it was concluded that the tetrahedrally coordinated aluminium, Al_T, content determined by ^{27}Al MAS NMR was the best available measure of acid-site concentration. ^{27}Al MAS NMR also showed that limited loss of Al_T with calcination below 1000 K was accompanied by the generation of non-framework tetrahedrally coordinated aluminium, Al_{NFT}, and non-framework octahedrally coordinated aluminium, Al_{NFO}. A pronounced loss of Al_T with calcination above 1000 K was accompanied by a concomitant increase in Al_{NFT}, whereas Al_{NFO} only increased slightly. The Al_T content of spent silica-bound catalysts was also determined following the present propane aromatisation experiments; no evidence was found for Al_T transfer to or from the framework structure during catalysis. It follows that decreases in activity with time on stream can be attributed to progressive poisoning by coke formation rather than to a depletion of acid sites through Al_T migration from the framework structure during reaction.

The activity for propane activation or aromatisation at 808 K is plotted against previously determined[13] values of Al_T in Fig. 9; values for propane activation on unbound and silica-bound catalysts are after 1 h on stream, whilst those for aromatisation are mean values from the three sets of analyses for each catalyst. Clearly activity depends on Al_T content, with a maximum for unbound HZSM-5 at *ca.* 3.0 Al_T atoms per unit cell and maxima for silica bound HZSM-5 at *ca.* 4.0 Al_T atoms per unit cell. Since the total number of Al atoms per unit cell is constant, an increase in activity to a maximum and a subsequent fall are expected with progressive structural dealumination, if active sites are the result of synergistic interactions between structural and extra-structural Al atoms. The shape of the plots in Fig. 9 suggests that there are such synergistic interactions between Al_T atoms and extrastructural Al_{NFT} and Al_{NFO} atoms in the present catalysts. In an attempt to confirm such synergism, the activity of unbound HZSM-5 for propane activation was plotted *vs.* $[Al_T] \times [Al_{NFT}]$ and $[Al_T] \times [Al_{NFT} + Al_{NFO}]$; neither plot was an acceptable straight line, although each showed that the activity increased with the product of the two concentrations. Thus, even with the best experimental data from the present research, it is not possible to confirm unequivocally that the strong acid sites necessary for propane conversion arise from synergistic interactions between structural and extrastructural aluminium atoms. Nevertheless, it has been shown that the activity of HZSM-5 catalysts for propane conversion can be maximised by control of the calcination conditions and that silica binding does not seriously impair catalytic activity.

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References

1 J. R. Mowry, R. F. Anderson and J. A. Johnson, *Oil Gas J.*, 1985, 128.
2 N. Y. Chen and T. Y. Yan, *Ind. Eng. Chem. Proc. Des. Dev.*, 1986, **25**, 151.
3 Y. Ono, *Catal. Rev.- Sci. Eng.*, 1992, **34**, 179.
4 H. Kitagawa, Y. Sendoda and Y. Ono, *J. Catal.*, 1986, **101**, 12.
5 N. S. Gnep, J. Y. Doyement, A. M. Seco, F. Ramoa Ribeiro and M. Guisnet, *Appl. Catal.*, 1988, **43**, 155.
6 P. Schultz and M. Baerns, *Appl. Catal.*, 1991, **78**, 15.
7 A. Corma, C. Goberna, J. M. Lopez Nieto, N. Parades and M. Perez, *Zeolite Chemistry and Catalysis*, ed. P. A. Jacobs, N. I. Jaeger, L. Kubdkova and B. Wichterlova, Elsevier, Amsterdam, 1991, p. 409.
8 A. Yu. Stakheev, A. Yu. Khodakov, L. M. Kustov, V. B. Kazansky and Kh. M. Minachev, *Zeolites*, 1992, **12**, 866.
9 B. S. Kwak and W. M. H. Sachtler, *J. Catal.*, 1994, **145**, 456.
10 B. S. Kwak, W. M. H. Sachtler and W. O. Haag, *J. Catal.*, 1994, **149**, 465.
11 R. W. Lago, W. O. Haag, R. J. Mikovsky, D. H. Olsen, S. D. Hellring, K. D. Schmitt and G. T. Kerr, *Proc. 7th Int. Conf. Zeolites*, ed. Y. Murakami, A. Iijima and J. W. Ward, Kodansha-Elsevier, Tokyo, 1986, p. 677.
12 Y. Sendoda and Y. Ono, *Zeolites*, 1988, **8**, 101.
13 R. Rudham and A. W. Winstanley, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 3191.
14 G. Spoto, S. Bordiga, G. Ricchiardi, D. Scarano, A. Zecchina and E. Borello, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 2827.
15 J. Bandiera and Y. Ben Taarit, *Appl. Catal.*, 1990, **62**, 309.

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