

# Bimolecular Hydrogen Transfer over Zeolites and SAPOs having the Faujasite Structure

John Dwyer,\* Khalid Karim and Adeola F. Ojo

Chemistry Department, UMIST, PO Box 88, Manchester M60 1QD, UK

Silica-rich Y zeolites prepared by primary or secondary synthesis and samples of SAPO-37 have been synthesized and characterized. These materials are then evaluated as catalysts for the transformation of cyclohexene. From product distributions at low conversion the relative rates of isomerization and bimolecular hydrogen transfer are measured and discussed in terms of active site density.

The transformation of hydrocarbons over acid-zeolite catalysts is a major route to liquid fuels such as gasoline. Of particular importance currently, is the control of product composition from liquid catalytic cracking (FCC) units to produce fuels which retain octane quality but show improved environmental characteristics. This development began with the elimination of lead from gasoline and incoming restrictions on aromatics and olefinic contents place further restrictions on refining operations.

The activation and conversion of hydrocarbons over zeolites is a subject of intense activity. Factors influencing the role of active sites have been reviewed recently,<sup>1</sup> as has the fate of carbocations in subsequent reactions, particularly in regard to FCC processing.<sup>2</sup> For a given feed, zeolite structure and composition the distribution of products depends upon process conditions and on the balance of the carbocation processes, in particular upon the balance of  $\beta$ -scission, isomerization and bimolecular hydrogen-transfer reactions. Recently it was demonstrated that cyclohexene transformation provides a suitable test reaction for the relative rates of isomerization and bimolecular hydrogen transfer, and results are found to correlate well with results for gas-oil cracking.<sup>3</sup> In general, bimolecular hydrogen transfer in the FCC process is considered to result in enhanced yields of gasoline but can result in reduced octane by converting alkenes and naphthenes into aromatics and alkanes. Consequently, factors influencing relative rates of carbenium-ion processes are of particular interest in the control of fuel-product compositions.

The present paper considers changes in the relative rates of isomerization and bimolecular hydrogen transfer arising from changes in the framework composition of a series of microporous catalysts having the same (faujasitic) structure. These catalysts include silica-rich Y zeolites produced by both primary and secondary synthesis and siliceous SAPO-37.

## Experimental

The CSY zeolites were prepared by treatment with ammonium hexafluorosilicate.<sup>4</sup> ZSM-20 was synthesized from gel using tetramethyl orthosilicate as the silica source.<sup>5</sup> The SAPO-37 materials were synthesized using TPA and TMA as templates.<sup>6</sup> The silicon content in the SAPO-37 was varied by varying the silica gel composition. The unit cell parameters and crystallinity were determined using a Philips PW1710 diffractometer following the ASTM method.<sup>†</sup> All the samples were good crystalline microporous materials with high surface areas (Table 1). <sup>29</sup>Si MAS NMR spectra of the zeolites were obtained using a Varian VXR-300 JEOL FT spectrometer at 59.6 MHz, by the Solid State NMR Unit at Durham University.

<sup>†</sup> ASTM D-3940-80.

Cyclohexene transformation was studied at 250 °C in a fixed-bed, stainless-steel, intermittent-flow reactor. The ammonium forms of the zeolites were activated in a nitrogen stream at 450 °C for 10 h. The SAPO-37 samples were calcined in an air stream at 500 °C in the reactor tube before activation in a nitrogen stream. The conversion of cyclohexene was altered by varying the flow of the feed, over a fixed volume of the fresh catalyst. Low conversion was obtained by diluting the zeolite with SiO<sub>2</sub> using ammonium-stabilized Ludox AS40 (Du pont, 40% SiO<sub>2</sub>).

## Results and Discussion

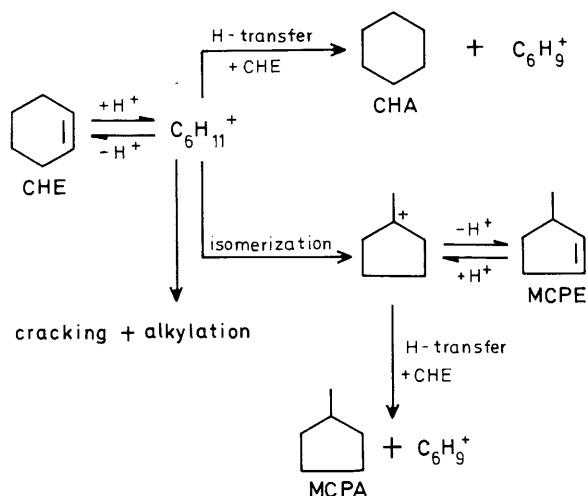
The transformation of cyclohexene over acidic zeolites gives cyclohexane, methylcyclohexane, methylcyclopentane and methylcyclopentene with traces of other products. Both methylcyclopentane and cyclohexane involve bimolecular hydrogen transfer and both five-ring products involve isomerization (Scheme 1). Consequently, it is possible to examine bimolecular hydrogen transfer, relative to isomerization, from yields at low conversion.<sup>3</sup> At higher conversion dimethylcyclopentane, dimethylcyclopentene, benzene and C<sub>1</sub>-C<sub>5</sub> products are observed along with some higher (C<sub>12</sub>) products. Typical results at conversions up to 15% are shown in Fig. 1.

The shape of these yield *vs.* conversion plots can indicate the type of product, primary, secondary *etc.*<sup>7</sup> Methylcyclopentene, produced by unimolecular isomerization, is a primary product for reaction over all the catalysts and is capable of further reaction *via* bimolecular hydrogen transfer to give the secondary product cyclopentane. Cyclohexane is present as a secondary product for reaction over CSY and NH<sub>4</sub>Y zeolites, but appears to be both a primary and a secondary product for reaction over SAPO-37. The initial product selectivity towards methylcyclopentene, cyclohexane and methylcyclopentane is taken as the slope of the appropriate yield curve at the origin ( $x \rightarrow 0$ ).

Table 1 Comparative properties of faujasite-type zeolites

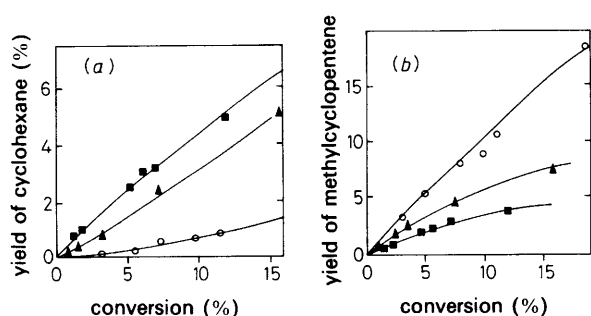
zeolite	cubic cell parameters, $a_0/\text{\AA}$	Si/Al (bulk)	crystallinity (%)	B.E.T. surface area/m <sup>2</sup> g <sup>-1</sup>
NH4Y	24.69	2.48	106	806
CSYI	24.64	2.85	110	830
CSYII	24.51	4.50	108	828
CSYIII	24.46	5.16	103	817
CSYIV	24.40	7.35	97	584
ZSM20 <sup>a</sup>	24.53 <sup>a</sup>	3.8	116	847
USY	24.30	7.5	70	756
SAPO-37A	24.48	0.35	105	850

<sup>a</sup> Assigned in cubic symmetry.



**Scheme 1** Reaction of cyclohexene over acidic zeolites: CHE, cyclohexene; MCPA, methylcyclopentane; CHA, cyclohexane; MCPE, methylcyclopentene

The relative rate of the monomolecular isomerization reaction to the rate of bimolecular hydrogen transfer over CSY zeolites increases with increasing framework Si/Al ratio or with decreasing unit-cell size (Tables 1 and 2). Agreement on the relative significance of factors controlling rates of bimolecular processes (H-transfer) *vs.* unimolecular processes (isomerization or  $\beta$ -scission) in acid zeolites is not complete, although several important features are recognized. Increased hydrogen transfer in the cracking of gas oil over Y zeolite catalysts is found to increase with the aluminium content of the zeolite framework, and hence increased unit-cell size. This result is interpreted in terms of site distribution.<sup>3</sup> It is presumed<sup>8</sup> that the bimolecular process requires proximate (aluminium) sites to facilitate hydrogen transfer between sorbed carbenium ions and alkenes (or alkanes), whereas isomerization or  $\beta$ -scission can occur on single sites. Consequently, as aluminium is removed from the framework, neighbouring sites are at increased distances of separation and hydrogen transfer is reduced relative to  $\beta$ -scission. Recent



**Fig. 1** Selectivity curves for cyclohexene transformation over  $\text{NH}_4\text{Y}$  ( $\blacktriangle$ ), CSY (Si/Al = 7.35) ( $\circ$ ) and SAPO-37 ( $\blacksquare$ ) for (a) cyclohexane and (b) methylcyclopentene

**Table 2** Catalytic conversion of cyclohexene at 250°C

zeolite	initial selectivity			isomerization
	MC pentene	MC pentane	C-hexane	H-transfer
NH4Y	0.491	0.234	0.285	1.40
CSYI	0.614	0.126	0.155	2.55
CSYII	0.850	0.180	0.110	3.80
CSYIII	0.772	0.069	0.103	4.80
CSYIV	0.860	0.055	0.092	6.20
ZSM20	0.790	0.071	0.125	4.30
USY	0.880	0.286	0.029	3.70

$$\frac{\text{isomerization}}{\text{H-transfer}} = \frac{\text{MC pentene} + \text{MC pentane}}{\text{C hexane} + \text{MC pentane}}$$

studies on hydrogen transfer, using cyclohexene as feed at 370°C, over dealuminated faujasites suggest that two sites within a single supercage are required for bimolecular hydrogen transfer between a sorbed cyclohexyl carbenium ion and a sorbed cyclohexene molecule.<sup>9</sup> This conclusion is based on the observation of a considerable decrease in H-transfer when the framework aluminium content falls to values where there are presumed to be fewer than one aluminium atom per supercage (<8Al per unit cell), although the distribution of Al is not known in any detail. In other work<sup>10</sup> it is clearly demonstrated that sorption effects are important. For example the H-transfer process in gas-oil cracking typically involves reaction between alkenes and carbenium ions and the sorption preference for alkenes *vs.* alkanes is very dependent upon the polarity of the internal zeolitic surfaces. As the aluminium content is reduced surface polarity is reduced and sorption of the less polarizable alkanes as compared to the (quadrupolar) alkenes becomes more favourable. Reduced relative concentrations of alkenes results in reduced bimolecular hydrogen transfer.

The importance of sorption effects *via* surface curvature<sup>11</sup> is unlikely to be significant in the present work since all of the zeolites are similar in structure. However, the influence of surface polarity and electrostatic field gradients<sup>12</sup> is clearly of importance here. Similarly there may be a role for site proximity in the explanation for results in Table 2. On the other hand, although it is likely that site proximity is related to aluminium concentration in Y zeolites, where there is only one type of crystallographic tetrahedral site<sup>13</sup> this simple generalization is not necessarily the case for all structures.

Results for SAPO-37 B with a very low silicon content show high hydrogen transfer relative to isomerization as compared to Y zeolite (Table 3). Increasing the silica content (SAPO-37 A) reduces the relative rate of hydrogen transfer (Table 3) as it does for the CSY zeolites (Table 2). SAPO-37 has the same (faujasitic) framework topology as Y zeolite and the higher relative H-transfer to isomerization function can be explained both in terms of the proximity of active sites in the aluminosilicate 'islands'<sup>14</sup> which are reported to exist in the structure and also in terms of sorptive effects. It is known

**Table 3** Catalytic conversion of cyclohexene over SAPO-37 and zeolite Y

zeolite	Si (%)	Si/Al ratio	initial selectivity			isomerization
			MC pentene	MC pentane	C-hexane	H-transfer
NH4Y		2.53	0.491	0.234	0.285	1.40
SAPO-37 A	6.6	0.35	0.34	0.245	0.41	0.90
SAPO-37 B	3.6	0.24	0.30	0.254	0.50	0.70

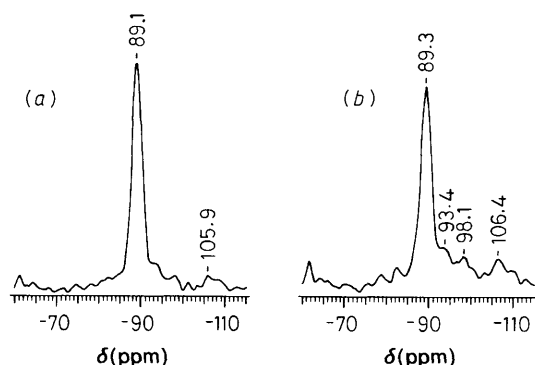


Fig. 2  $^{29}\text{Si}$  MAS NMR spectra of (a) SAPO-37(B) and (b) SAPO-37(A)

that the second coordination sphere of the aluminium atoms, which can influence site activity,<sup>13</sup> is dependent on the composition of the faujasitic aluminosilicate 'islands' in the SAPO-37 framework,<sup>14</sup> so that increasing Si/Al in SAPO-37 should parallel results in Y zeolites, as is observed. The role of sorption may be of particular importance in SAPO-37 since strong preference is reported<sup>15</sup> for some polar sorbates.

Some insight into the present results for SAPO-37 is available from  $^{29}\text{Si}$  MAS NMR spectra (Fig. 2). Results show an intense peak at  $-89.1$  ppm and a weak peak at  $-105.9$  ppm. The peak at  $-89.1$  ppm corresponds, in faujasitic zeolites, to silicon atoms linked *via* oxygen atoms to four aluminium atoms. As the silicon content is increased (SAPO-37 A) the major peak, now at  $-89.3$  ppm, corresponding to Si(4Al) is accompanied by smaller peaks at  $-93.5$ ,  $-98.2$  and  $-106.4$  ppm. Peaks with similar chemical shifts are assigned to Si(4Al), Si(3Al), Si(Al) and Si(0Al) in faujasitic zeolites.<sup>16</sup> Relative intensities of NMR signals for the different silicon coordinations [Si(*n*Al)] and associated chemical shifts for SAPO-37 and ammonium Y zeolite are compared in Table 4. Clearly silicon exists in multiple chemical environments in SAPO-37 A in keeping with the existence of aluminium atoms in more isolated (less clustered sites). Consequently, increasing silicon in SAPO-37 has an effect similar to that in Y zeolite. Site activity, as reflected in isomerization or  $\beta$ -scission, is increased and bimolecular hydrogen transfer is decreased.

Zeolite ZSM-20 is a silicon-rich zeolite which may be synthesized directly.<sup>17</sup> It has 12-ring pores and the structure is faujasitic but tends to be a mixture of both the cubic form (as in Y zeolite) and the hexagonal form.<sup>18,19</sup> The present work shows, at least for the relative rates of hydrogen transfer and isomerization (Fig. 3), that results are broadly in line with those for the CSY zeolites, although hydrogen transfer may be slightly increased relative to isomerization. Additionally, results for a US-Y-type zeolite with framework composition  $[(\text{AlO}_2)_{13}(\text{SiO}_2)_{179}]$  prepared by steaming CSY (III) at  $600^\circ\text{C}$  for 7 h are shown in Fig. 3. The hydrogen transfer/isomerization ratio is out of line with results for CSY zeolites but is close to a value reported recently<sup>3</sup> for steamed REY

Table 4  $^{29}\text{Si}$  MAS NMR data: distribution of Si(*n*Al) coordination relative intensity

zeolite	Si4Al	Si3Al	Si2Al	Si1Al	Si0Al
NH4Y	1.63	12.3	42.4	33.7	10.7
	(-85.1)	(-89.4)	(-94.7)	(-100.3)	(-105.5)
SAPO-37 A	73	13	7.6	—	6.4
	(-89.3)	(-93.5)	(-98.1)	—	(-106)
SAPO-37 B	95.1	—	—	—	5.0
	(-89.1)	—	—	—	(-106)

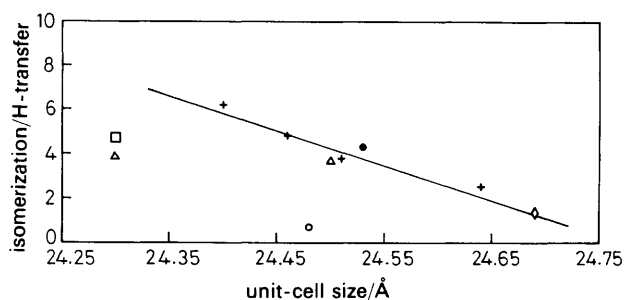


Fig. 3 Isomerization/hydrogen transfer as a function of zeolite unit-cell size:  $\diamond$ , NH<sub>4</sub>Y; +, CSY; \*, ZSM-20;  $\square$ , USY;  $\circ$ , SAPO-37;  $\triangle$ , REUSY<sup>3</sup>

zeolite. Steaming tends to increase hydrogen transfer relative to isomerization and this cannot be explained in terms of framework site proximity since steaming reduces framework aluminium content and unit-cell size. However, present results are consistent with a proposed role for non-framework aluminium species in enhancing hydrogen transfer,<sup>3</sup> although changes in sorption effects may also be significant.<sup>2</sup>

## Conclusion

In a series of aluminosilicate zeolites having the same (faujasitic) structure the ratio of isomerization activity to bimolecular hydrogen transfer activity for cyclohexene conversion decreases with increasing unit-cell size (increased aluminium content). Results for the silico-aluminophosphate (SAPO-37) show particularly low values for the relative rates of isomerization/bimolecular hydrogen transfer which are significantly lower than for aluminosilicates of similar cell size. The synthesized silica-rich zeolite ZSM-20 gives results similar to those for silica-rich faujasites prepared by secondary synthesis to have a similar framework composition Si/Al. These results are consistent with the role of site density in bimolecular hydrogen transfer, although a role for sorptive effects cannot be excluded. Results for SAPO-37 are consistent with the proposal that islands of aluminosilicate are present within the (faujasitic) structure of this material.

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