

10 Application of Molecular Sieve Zeolites to Catalysis

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In the past decade the subject of catalysis has been discussed in Annual Reports on three occasions.¹ In 1964 and 1968, aspects of catalytic reactions over metals were considered, and in 1966 the topic was homogeneous catalysis by complexes of Group VII elements. The present report will review some of the work that has been published concerning the role that crystalline molecular sieve zeolites have played in the catalytic reactions of hydrocarbons.

This area of research has undoubtedly been one of the major growth points in catalysis during the last decade. The application of zeolites as catalysts for various processes in the petroleum refining industry was discovered during the 1959–62 period soon after the Union Carbide Corporation began to produce synthetic Linde molecular sieves on a large commercial scale. The upsurge in publication of papers since that period emphasizes the importance of these materials. At the 1st international conference on zeolites in London in 1967, Milton estimated² that over 60% of installed catalytic cracking capacity in the United States employed zeolite-based catalysts, and in 1970 Arey³ suggested that the figure had risen to approximately 90% for fluid catalytic cracking units. Weisz⁴ has compared the industrial impact of the zeolite catalyst to that of the Haber ammonia and Ziegler–Natta polymerization catalysts that produced Nobel prizes for catalytic science, and Weisz quotes the annual consumption of zeolite-containing catalysts for petroleum cracking as > 100 000 tons.⁴

The catalytic application of zeolites is a topic that has been well served by review articles in the past few years.^{5–9} At the 2nd international conference on zeolites in Worcester, U.S.A., in 1970 there were two authoritative, invited papers by Venuto¹⁰ and by Rabo and Poutsma.¹¹ The former paper classified

¹ G. C. Bond, *Ann. Reports*, 1964, **61**, 99; 1966, **63**, 27; *Ann. Reports (A)*, 1968, **65**, 121.

² R. M. Milton, in 'Molecular Sieves', Society of Chemical Industry, London, 1968, p. 199.

³ W. F. Arey, jun., *Oil and Gas J.*, 1970, **68**, 64.

⁴ P. B. Weisz, *Ann. Rev. Phys. Chem.*, 1970, **21**, 175.

⁵ Kh. M. Minachev, V. I. Garanin, and Ya. I. Isakov, *Russ. Chem. Rev.*, 1966, **35**, 903.

⁶ J. Turkevich, *Catalysis Rev.*, 1968, **1**, 1.

⁷ P. B. Venuto and P. S. Landis, *Adv. Catalysis*, 1968, **18**, 259.

⁸ F. G. Ciapetta, *Chimica e Industria*, 1969, **51**, 1173.

⁹ Kh. M. Minachev, *Kinetika i Kataliz*, 1970, **11**, 413.

¹⁰ P. B. Venuto, *Adv. Chem. Ser.*, 1971, No. 102, 260.

¹¹ J. A. Rabo and M. L. Poutsma, *Adv. Chem. Ser.*, 1971, No. 102, 284.

many of the organic reactions that had been observed over zeolite catalysts, whereas the latter paper considered in more detail the structural and mechanistic aspects of zeolite catalysts, with particular reference to the cracking of cumene and hexane. In the present Report some of the important arguments arising out of these articles will be discussed and attention drawn to a number of important papers that have appeared in the past two years.

1 Structure of Zeolites

The catalytic properties of zeolites are very closely related to their unique crystal structures. These structures provide the following features: (i) a three dimensional lattice containing uniform pores of molecular dimensions, (ii) a high surface area which is only accessible to molecules able to diffuse through the porous network, and (iii) excellent thermal stability at relatively high temperatures. In view of this correlation between structure and catalytic properties it is necessary to discuss briefly some of the more important structural details of zeolites.

The origin of the events leading to the discovery of zeolite catalysts lies in inorganic chemistry and crystallography rather than in catalysis itself. Much of the early work on the structure of naturally-occurring zeolitic minerals and the synthesis of zeolite materials was done by Barrer and his colleagues. The articles by Barrer,¹² and also by Breck,¹³ summarize much of the information concerning the classification and detailed structure of these materials. In order to analyse catalytic results, it is essential to be aware of the zeolite framework structure, and also to obtain as much information as possible concerning the location of cations and water molecules within the zeolite lattice.

X, Y, and Faujasite.—The X and Y zeolites are the most widely used in catalytic studies (in various modified forms). Both are synthetic forms of an aluminosilicate framework which has the same topology as the naturally-occurring mineral faujasite. Turkevich⁶ has described in detail the structure of these materials.

The primary structural unit in the faujasite structure is the so-called sodalite cage, or β -cage, which is a truncated octahedron containing 24 silicon (or aluminium) tetrahedra. It is composed of six four-membered rings and eight six-membered rings (rings of four or six oxygens respectively, joined *via* silicon or aluminium), and has a free diameter in the cavity of approximately 0.66 nm. The pore opening of a four-membered ring is too small to be important in catalytic terms but that of a six-membered ring is 0.22 nm, which is sufficient to permit the entry of some molecules. The three-dimensional, open, porous structure of the faujasite is derived by the joining of these sodalite cages in a tetrahedral arrangement through hexagonal prisms, with each such prism being joined to a six-ring face of a sodalite cage. Thus a hexagonal prism will be composed of two parallel six-ring faces and six four-membered sides.

¹² R. M. Barrer, *Endeavour*, 1964, **23**, 122.

¹³ D. W. Breck, *J. Chem. Educ.*, 1964, **41**, 678.

The joining of the sodalite cages in this manner produces the characteristic faujasite cage (often referred to as the α -cage or supercage) which is the major cavity in the zeolite structure. The cage is a 26-hedron made up of eighteen four-membered rings, four six-membered rings, and four twelve-membered rings. These latter rings are arranged as the four sides of a tetrahedron and afford the most important entry points into the cavity. The free diameter within the supercage is approximately 1.30 nm, but the diameter of the pore opening is 0.80–0.90 nm, which is sufficient to permit entry of aromatic compounds and some branched-chain hydrocarbons. The capacity of the supercage for a variety of molecules has been listed⁶ and ranges from 28 molecules of water to 2.1 molecules of perfluorodimethylcyclohexane.

Meier¹⁴ classified the structural frameworks of faujasite and many of the other naturally-occurring zeolites in great detail, and more recently¹⁵ stereograms of these structures have appeared. In the latter paper, the skeletal framework drawings were based on the T-atoms (Si or Al), with the T—O—T bridges represented by straight lines. The drawings were constructed as stereopairs and the stereoscopic representation was arranged so that the selected viewing direction clearly indicated the main channels in the particular zeolite class.

Smith¹⁶ has tabulated the T—O distances and T—O—T angles for a variety of hydrated and dehydrated ionic forms of the faujasite-type structure. The location of the cations in X and Y zeolites has been the subject of intense activity and speculation. In the mid-60's, three main types of site were generally recognized, i.e. type S_I located in the hexagonal prisms between the sodalite units, type S_{II} located in the open six-membered faces of the sodalite unit, and type S_{III} located on the walls of the cavity. As single-crystal samples became available, and X-ray diffraction data more precise, the number of defined cation sites increased, and for a time there was a degree of confusion about the nomenclature. However the nomenclature adopted by Smith (illustrated in Figures 1 and 2 of reference 16) has now been adopted by the majority of workers in the field. It is as follows: site I situated in the centre of the hexagonal prism; site I' on a triad axis displaced into the sodalite cage from the hexagonal face shared by the sodalite cage and the hexagonal prism; site II' on a triad axis displaced into the sodalite cage from the open (unshared) six-membered ring of the sodalite unit; site II and site II* displaced (slightly and considerably, respectively) from this ring into the supercage; site III displaced into the supercage from bridging four-membered rings; and site V very nearly at the centre of the twelve-membered rings separating the supercages.

These well-defined locations are the positions that the cations required to compensate for the excess negative charge arising out of the silicon–oxygen–aluminium skeleton will occupy. When first synthesized, zeolites are usually in the sodium form, and there will be an equivalent number of univalent sodium cations to 'framework' aluminium to establish electrical neutrality within the

¹⁴ W. M. Meier, in 'Molecular Sieves', Society of Chemical Industry, London, 1968, p. 10.

¹⁵ W. M. Meier and D. H. Olson, *Adv. Chem. Ser.*, 1971, No. 101, 155.

¹⁶ J. V. Smith, *Adv. Chem. Ser.*, 1971, No. 101, 171.

material. It is a well-known feature of zeolites that they undergo ion exchange, with the sodium cations being replaced by a variety of other cationic species. As will be discussed later, such cation exchange can have a profound effect upon the catalytic activity of the zeolite species.

Rees¹⁷ has given a very comprehensive report on the phenomenon of ion exchange in zeolites, both from the viewpoint of equilibrium and kinetic studies. Barrer and Rees,^{18,19} and Sherry,²⁰ have very thoroughly investigated the ion-exchange equilibria in X and Y zeolites. A recent article by Sherry²¹ is another major contribution to this topic.

The location of the exchanged cations will be of vital importance in catalytic studies. Table 1 in reference 17 gives an excellent summary of the position regarding the site occupancy of a variety of cation-exchanged faujasites, both in the hydrated and dehydrated forms. The bulk of this data was acquired by X-ray diffraction techniques, with the work of Bennett and Smith,²² and of Olson and colleagues²³ being particularly prominent. A recent paper²⁴ has added to the knowledge of the location of the cations in highly-exchanged cerium-X zeolites. It has been reported that in the hydrated sample the cerium cations were distributed between sites II and I', and on dehydration in air at 813 K cation migration to I and I' sites took place, with a site occupancy of 0.74 quoted for I' after dehydration. It should be remembered that the X-ray diffraction techniques actually yield maps of electron density which are subjectively analyzed. With the complex situation present in cation-exchanged zeolites, the quoted precision of the data regarding the cation distributions should always be treated with caution. However, there can be little doubt in general concerning the different distributions that have been observed (dependent upon the nature of the cation), or the manner in which such distributions can be altered on dehydration.

As previously mentioned, both the X and Y synthetic zeolite forms are similar to that of faujasite. Their main difference lies in the relative Si to Al content. In the X-type material, the composition can be represented by the general formula $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}], 264\text{H}_2\text{O}$ with a Si:Al ratio of about 1.2, whereas the Y-type material has the general formula of $\text{Na}_{56}[(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}], 264\text{H}_2\text{O}$ with a Si:Al ratio of about 2.4, similar to that of naturally-occurring faujasite. A necessary consequence of the higher aluminium content of the X zeolites, relative to the Y-type, is that they have an appreciably higher cation density.

Mordenite, Erionite, and Offretite.—A considerable amount of work has been published concerning the catalytic properties of modified forms of mordenite.

¹⁷ L. V. C. Rees, *Ann. Reports (A)*, 1970, **67**, 191.

¹⁸ R. M. Barrer, J. A. Davies, and L. V. C. Rees, *J. Inorg. Nuclear Chem.*, 1968, **30**, 3333; 1969, **31**, 2599.

¹⁹ R. M. Barrer, L. V. C. Rees, and M. Shamsuzzoha, *J. Inorg. Nuclear Chem.*, 1966, **28**, 629.

²⁰ H. S. Sherry, *J. Phys. Chem.*, 1966, **70**, 1158.

²¹ H. S. Sherry, *Adv. Chem. Ser.*, 1971, No. 101, 350.

²² J. M. Bennett and J. V. Smith, *Materials Res. Bull.*, 1969, **4**, 343, and earlier papers.

²³ D. H. Olson, *J. Phys. Chem.*, 1970, **74**, 2758; and earlier papers.

²⁴ F. D. Hunter and J. Scherzer, *J. Catalysis*, 1971, **20**, 246.

Some recent interest has also been centred on synthetic zeolites related to the naturally-occurring erionite and offretite minerals. Consequently it is necessary to consider briefly these structures, which are appreciably different from that of faujasite.

The structure of the fully hydrated form of mordenite was originally determined by Meier.²⁵ It is one of the most silica-rich zeolites known, with a Si:Al ratio of ca. 5. The idealized unit cell composition corresponds to a general formula of $\text{Na}_8[(\text{AlO}_2)_8(\text{SiO}_2)_{40}]\cdot 24\text{H}_2\text{O}$. The structure contains none of the cubic symmetry of the faujasite structure and is, in fact, orthorhombic. A particular feature is the importance and predominance of five-membered rings, and the mordenite framework can be constructed from a chain-like sequence of tetrahedra which can be cross-linked to other identical chains. Such chains run parallel to the *c* axis of the unit cell, and enclose wide parallel, near-elliptical channels (with free diameter 0.59×0.70 nm) which are circumscribed by puckered twelve-membered rings. These main channels in the mordenite are linked by additional pockets which can be entered through an eight-membered ring. These orifices have a free diameter of about 0.28 nm, so they can accommodate a limited number of molecules (smaller than *n*-butane). There are, however, effectively no interconnecting channels in mordenite, as these side channels have restrictions which essentially prohibit transfer of molecules from one main channel to another. The pore structure of mordenite does not therefore have the three-dimensional character of the X and Y zeolites. Another difference which can have important catalytic consequences is that with highly-siliceous zeolites such as mordenite, all the exchangeable cations can be directly replaced by H^+ ions by treatment with dilute acid without destroying the lattice framework. Some of the cations have been located in the side pockets and others are considered to be in the main channels of the pore system. However, the cation distribution in mordenite has not been determined in as detailed a manner as for the faujasite materials.

Offretite and erionite are both members of the chabazite group of naturally-occurring zeolites, and are hexagonal. There has been considerable confusion in the literature concerning their structure and they were originally considered identical. Bennett and Gard,²⁶ however, showed that the '*c*' spacing in offretite was half that in erionite. Both species can be regarded as layer structures with the primary building units being hexagonal prisms and single hexagons, but they differ in their stacking sequence. In erionite, layer A consists of six-membered rings with layer B being hexagonal prisms. The next layer of six-membered rings, layer C, is rotated through 60° relative to layer A, and the resultant stacking sequence is ABCBABCB. In offretite all the layers of six-membered rings are superimposed and therefore identical. Consequently the stacking sequence for offretite along the *c* direction is ABAB. A paper by Whyte *et al.*²⁷ illustrates

²⁵ W. M. Meier, *Z. Krist.*, 1961, **115**, 439.

²⁶ J. M. Bennett and J. A. Gard, *Nature*, 1967, **214**, 1005.

²⁷ T. E. Whyte, jun., E. L. Wu, G. T. Kerr, and P. B. Venuto, *J. Catalysis*, 1971, **20**, 88.

clearly the manner in which large cavities are built up by such stacking arrangements in both erionite and offretite.

A consequence of the difference in the structures is that offretite is considerably more open than erionite, and contains channels with a free diameter of 0.63 nm. The absorptive capacity (a property closely-associated with catalytic activity) of offretite will thus be considerably higher than that of erionite, although only a small degree of stacking disorder will considerably constrict the channel widths in offretite. Gard and Tait²⁸ reported that there were two different types of cation site, located on the axes parallel to *c* of the single six-membered rings and the large channels, which were readily ion exchanged. Electron microscopy, together with X-ray diffraction results,²⁹ has provided further information concerning the cation distribution in unfaulted offretite, and has further indicated the effect upon the adsorption properties of the size of the cation in the main channel.

Synthetic preparations of both offretite and erionite have been reported, and in several instances their catalytic properties examined. Some of the recent types of synthetic zeolites have been reported³⁰ to have similar structures to those just discussed. Zeolite T has been shown to have a similar structure to offretite,²⁸ and the structure of zeolite L³¹ is based on similar polyhedral cages to those found in erionite and offretite. Such new zeolitic species are likely to have useful and interesting catalytic properties, but as yet only a very limited amount of published work has appeared on such aspects of these materials.

2 Catalytic Activity of Zeolites

Undoubtedly the major application of zeolites in catalytic fields has been in the area of hydrocarbon cracking. Another growing use is in hydrocracking processes, which give the refiner added flexibility in oils which can be processed and products which can be made. However, zeolites have also been used as catalysts in a great number of other very important hydrocarbon reactions. Venuto and Landis⁷ have surveyed the very prolific research literature of the 1960–68 period, and have clearly demonstrated the diversity of organic reactions studied. More recently, Venuto³² has listed some 50 important organic reactions that workers in the Mobil laboratories have shown to be catalytically affected by zeolites to a greater or lesser degree. In the limited space available here, attention will be focussed on some of the more important industrial reactions such as cracking, alkylation, dealkylation, isomerization, and oxidation, with particular attention being paid to recent publications in these areas.

Cracking Reactions.—Since the discovery³³ that the Na-X zeolite exhibited an activity for hydrocarbon cracking similar to that of the most active silica-alumina

²⁸ J. A. Gard and J. M. Tait, *Adv. Chem. Ser.*, 1971, No. 101, 230.

²⁹ R. Aiello, R. M. Barrer, J. A. Davies, and I. S. Kerr, *Trans. Faraday Soc.*, 1970, **66**, 1610.

³⁰ D. W. Breck, *Adv. Chem. Ser.*, 1971, No. 101, 1.

³¹ R. M. Barrer and H. Villiger, *Z. Krist.*, 1969, **128**, 352.

³² P. B. Venuto, *Chem. Tech.*, 1971, **1**, 215.

³³ P. B. Weisz and V. J. Frilette, *J. Phys. Chem.*, 1960, **64**, 382.

catalyst, there has been a vast amount of published work on this subject. The product pattern from Na-X was similar to that of the radical-controlled mechanism, and not to that obtained on the typical acidic catalyst. However, when it was established that further enhancement of the cracking activity was exhibited by Ca-X, and with a typical acidic cracking pattern of products, a whole range of unusually acidic catalysts was rapidly developed. There is now very little doubt that in this particular type of reaction the operation of the zeolite catalyst is best explained in terms of the formation of carbonium ion intermediates at acid sites on the internal surface. The mechanism of hydrocarbon cracking is assumed to involve the initial formation of a carbonium ion (C_nH_{2n-1})⁺ on the acid site, after which each transformation event regenerates a carbonium entity. With alkane cracking this entity could be formed either from the addition to the hydrogen (proton) of a Brønsted acid site of some olefinic thermally-produced species, or from the action of Lewis acid sites where the vacant electron pair orbitals would be satisfied by the abstraction of a hydride ion, *i.e.* hydrogen atom plus electron, from the alkane species. Even now it is experimentally difficult to differentiate between these two alternatives. From the large amount of work reported on the study of acidity in zeolite cracking catalysts, the Brønsted acidity would appear to be the important controlling factor. However, there are numerous examples where the importance of the Lewis type of acidity has also been demonstrated.

Much of the early work relating to the carbonium ion activity has been summarized by Rabo and Poutsma.¹¹ The work has indicated that (i) the locus of activity is on the intracrystalline zeolite surface, as demonstrated by the molecular sieve phenomenon, (ii) bi- and multi-valent cations induce high carboniogenic activity in X and Y zeolites, (iii) the decationized Y, obtained through heat treatment of NH₄-exchanged Y, had enhanced activity relative to the cation-exchanged Y zeolites, (iv) comparable forms of Y are more active and in certain forms more stable than X-type zeolites, and (v) loading of small amounts of noble metal by cation exchange greatly enhances the catalytic activity.

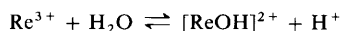
Perhaps the most successful cracking catalysts have been those using the rare-earth faujasite-type exchanged zeolites. These materials have a particularly high thermal and hydrothermal stability, are not subject to poisoning by metal impurities in the raw material, and have a high selectivity. Their success can in part be attributed to the peculiarity in reaction selectivity they exhibit, rather than to the capability of attaining higher reaction velocities; the ratio of medium molecular weight (liquid) range to gaseous range hydrocarbon products is very favourable. In this connection there has recently been a marked increase in the industrial importance of rare-earth elements, and it has indeed been reported³⁴ that the major employment of rare-earth elements is now in cracking catalysts.

Hirschler³⁵ proposed that the source of carboniogenic activity in acidic zeolite catalysts was the hydroxyl protons, and that the exchanged cations influenced

³⁴ R. L. Koffler, Proc. 7th Rare Earth Research Conference, 1968, vol. 2, p. 697.

³⁵ A. E. Hirschler, *J. Catalysis*, 1963, 2, 428.

the geometry and acidity of such protonic sites. Planck³⁶ also suggested the role of the hydroxyl proton in the carboniogenic activity, and postulated that hydrolysis of the cation produced the protons:



Consequent to this, Ward³⁷ showed that the ionic strength of the cation would control the amount of hydroxyl introduced, either through hydrolysis during cation exchange or by ionization of water upon activation. Therefore, if the catalytic activity is dependent upon hydroxyl concentration, then it will parallel the cation strength: there are various reports of such a correlation. Ward³⁷ observed that the catalytic cracking of cumene by decationized Y was accompanied by major changes in the i.r. spectrum of the catalyst, particularly in the absorption bands associated with the hydroxy-groups. The literature concerning i.r. spectroscopic studies of zeolites has recently been reviewed,³⁸ and this technique has been used extensively to examine the nature and location of hydroxy-groups. The acidity of cation-exchanged zeolites has also been examined using basic molecules such as ammonia, pyridine, and piperidine as probes. These molecules have the property that their interaction with Brönsted acid sites, with Lewis acid sites, with cations, and their hydrogen-bonding interactions give rise to different species detectable by i.r. spectroscopy. The series of papers by Ward on the nature of active sites on zeolites is an excellent example of the application of i.r. spectroscopy. In the latest of these³⁹ it has been reported that the transition-metal-Y zeolites display only protonic acidity, with no detectable Lewis acidity, after calcination at 753 K.

One of the standard test reactions for the characterization of cracking catalysts is the cracking (or dealkylation) of cumene, and Rabo and Poutsma¹¹ have summarized many of the early papers concerned with this reaction. It is of the Friedel-Crafts type, and is normally rationalized in terms of proton attack at an aromatic carbon atom with displacement of the side chain as a carbonium ion.⁷ Apart from kinetic data for the cumene cracking, differing product distributions are also observed, e.g. after calcination at 823 K, La-Y was more active than Ca-Y, and the C₃ fraction over La-Y contained a higher proportion of propane.

Eberly and Kimberlin⁴⁰ have examined the cumene-cracking activity of a series of single-component rare-earth Y-type zeolites, and correlated their findings with i.r. data. They noted an hydroxyl vibration in the range 3470–3520 cm⁻¹, characteristic of the rare earth, and which increased linearly with ionic radius. From pyridine adsorption effects it was concluded that the Brönsted acidity also increased slightly with ionic radius, although it was affected more by the calcination conditions. Lower calcination temperatures produced greater acidity, and

³⁶ C. J. Planck, in 'Proceedings of the 3rd International Congress on Catalysis,' Amsterdam, 1964, p. 727.

³⁷ J. W. Ward, *J. Catalysis*, 1968, **10**, 34; **11**, 238, 259.

³⁸ J. W. Ward, *Adv. Chem. Ser.*, 1971, No. 101, 380.

³⁹ J. W. Ward, *J. Catalysis*, 1971, **22**, 237.

⁴⁰ P. E. Eberly, jun. and C. N. Kimberlin, jun., *Adv. Chem. Ser.*, 1971, No. 102, 374.

also more-active cumene-cracking catalysts. However, they stated that changes in Brönsted acidity could not explain all the nuances of catalytic activity observed.

Otouma *et al.*,⁴¹ in a study of the cumene-cracking activity of hydrogen-, calcium-, and lanthanum-exchanged X and Y zeolites, reported that both the number and strength of acid sites in the zeolites increased with increasing extent of exchange. The catalytic activity could be correlated more readily with acid strength than with total acidity. Turkevich and Ono⁴² examined the cumene-cracking activity of a Y zeolite that had been partially exchanged with NH_4^+ , and also contained 2–3.5% by weight of Pd. The catalyst was active up to a pretreatment temperature of 773 K, but a sharp drop in activity was observed at greater pretreatment temperatures. From the effects of quinoline poisoning (titration) they concluded that the cumene-cracking activity was due entirely to Brönsted acid sites. In the same paper the cracking of 2,3-dimethylbutane was also examined, and it appeared that a small number of Lewis acid sites were necessary to initiate this reaction.

A study⁴³ on the quinoline poisoning of cumene-cracking activity, for Ce-Y, Ca-Y, and NH_4 -Y zeolites, has shown that a minimum dose of approximately one quinoline molecule per supercage was sufficient, and that there was a correlation between quinoline adsorption and poisoning. The effects were considered to arise mainly from blockage of the supercages, and to some extent the interpretation was at variance with the view of Turkevich that quinoline was a specific poison for Brönsted acid sites. Earlier studies had found⁴⁴ that the amount of quinoline required to poison the cumene-cracking activity of an Ag-Y zeolite correlated reasonably well with the expected number of surface hydroxyl species.

The cumene-cracking activity of a series of exchanged Y zeolites has been described,⁴⁵ and the relative activity found was $\text{La-Y} > \text{NH}_4\text{-Y} > \text{Ca-Y} > \text{Na-Y}$. The extent of conversion increased with increasing cation exchange, and the major products below 773 K were benzene and propylene. Also examined was the effect of altering the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio. With the Ca-Y zeolite, the cracking activity appeared to pass through a maximum as the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio was increased (the maximum occurring at about 4.6), whereas with the NH_4 -Y a steady increase was observed.

Topchieva *et al.*^{46–50} have also examined the role of cations in Y zeolites, and the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio, in respect of cumene-cracking activity. They observed the promoting effect of surface hydration and suggested that the active centres for cracking were surface hydroxy-groups where the H atom is protonized.

⁴¹ H. Otouma, Y. Arai, and H. Ukihashi, *Bull. Chem. Soc. Japan*, 1969, **42**, 2449.

⁴² J. Turkevich and Y. Ono, *Adv. Chem. Ser.*, 1971, No. 102, 315.

⁴³ M. S. Goldstein and T. R. Morgan, *J. Catalysis*, 1970, **16**, 232.

⁴⁴ J. T. Richardson, *J. Catalysis*, 1967, **9**, 182.

⁴⁵ K. Tsutsumi and H. Takahashi, *Seisan-Kenkyu*, 1969, **21**, 455, 457.

⁴⁶ K. V. Topchieva and Ho Chi Thanh, *Neftekhimiya*, 1970, **10**, 525.

⁴⁷ K. V. Topchieva and Ho Chi Thanh, *Doklady Akad. Nauk S.S.S.R.*, 1970, **193**, 641.

⁴⁸ K. V. Topchieva and Ho Chi Thanh, *Kinetika i Kataliz*, 1970, **11**, 490.

⁴⁹ K. V. Topchieva and E. N. Rosolovskaya, *Zhur. fiz. Khim.*, 1970, **44**, 870.

⁵⁰ K. V. Topchieva and Cho Shi Thuong, *Doklady Akad. Nauk S.S.S.R.*, 1971, **198**, 141.

They rationalized the observation that the cation-exchanged zeolites were more active than the decationized forms by suggesting that the incorporation of multivalent cations would stabilize the hydroxy-groups against thermal deactivation. The thermal stability of the active centres was higher for zeolites with large $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratios, and it was reported that dealumination increased the cracking activity. No simple direct relationship between aluminium content and catalytic activity was noted, but maximum activity corresponded to the situation when about 50% of the aluminium had been removed from the zeolite lattice. The fact that La-Y was more active than Ca-Y was attributed to differences in the cation locations of the respective zeolites. It has been reported¹¹ that the Ca^{2+} ions exhibit a preference for the hidden type I sites in the hexagonal prisms, whereas the trivalent rare-earth ions have a tendency to occupy positions in the sodalite cage.

The advantage of a high silica content in the zeolite is one of the prime reasons for the relatively recent upsurge in the catalytic applications of synthetic mordenite. Burbidge *et al.*⁵¹ have indicated the growing role that mordenite-type zeolites are playing in the petroleum industry as catalysts (and as adsorbents). In general, mordenite catalysts display a high initial activity, but activity maintenance is often relatively poor. By varying the synthesis conditions mordenites can be prepared with differing structural and adsorptive properties. Such mordenites have been classified⁵² as 'large-pore' or 'small-pore', depending on their ability to adsorb large molecules such as benzene and cyclohexane. Further varieties of mordenite, with differing adsorptive properties, can be produced by removing aluminium from the mordenite lattice structure by strong acid treatment, e.g. with HCl.⁵³

Eberly and Kimberlin⁵⁴ have compared the cumene-cracking activity of an H-mordenite sample, with a conventional $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 12, with that of a highly aluminium-deficient mordenite ($\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 64). The activity (A) of both catalysts decreased with time at temperatures above 500 K according to the relationship $A = at^n$, where n was approximately -0.5 . The aluminium-deficient mordenite was considerably more active, and this was mainly attributed to the larger adsorption capacity and the greatly decreased resistance to adsorptive diffusion.

A paper by Weiss and co-workers⁵⁵ reports further studies on cumene cracking over aluminium-deficient large-pore mordenites. In this case the alumina content (on an anhydrous basis) was reduced in stages from 11.2% (corresponding to the conventional H-mordenite) to an ultimate value of 0.1%. In this latter sample the Si:Al ratio was extremely high (of the order of 600), and it corresponded essentially to a silicic acid composition with a mordenite crystal-lattice.

⁵¹ B. W. Burbidge, I. M. Keen, and M. K. Eyles, *Adv. Chem. Ser.*, 1971, No. 102, 400.

⁵² L. B. Sand, in 'Molecular Sieves', Society of Chemical Industry, London, 1968, p. 71.

⁵³ L. I. Piguzova, E. N. Prokof'eva, M. M. Dubinin, N. R. Bursian, and Yu. A. Shavandin, *Kinetika i Kataliz*, 1969, **10**, 315.

⁵⁴ P. E. Eberly, jun. and C. N. Kimberlin, jun., *Ind. and Eng. Chem. (Product Res. and Development)*, 1970, **9**, 335.

⁵⁵ H. S. Bierenbaum, S. Chiramongkol, and A. H. Weiss, *J. Catalysis*, 1971, **23**, 61.

However, it still contained sufficient Brönsted acid exchange sites to be an active cracking catalyst. The initial activity of this material was lower than that of the less-dealuminated samples, but it had an appreciably lower rate of activity decline, so that after a short time on-stream it became the most active catalyst. It was suggested that the essential nature of the catalytically active site, *i.e.* the Brönsted acid site, was not altered by the removal of such a drastic quantity of alumina. The explanation of the improved lifetime of the low-alumina mordenite was that the low density of acid sites would reduce the rate of formation of higher molecular weight condensation products (capable of blocking the mordenite channel system). Further, the more-open pore structure would facilitate the desorption of such heavy products.

The removal of structural aluminium from Y zeolites also leads to improved thermal properties. An important, and still somewhat controversial, topic in this context is the production of so-called ultrastable faujasite.⁵⁶ The preparation involved specific thermal treatment of an Na-Y zeolite in which virtually all the sodium had been replaced by NH_4^+ by ion exchange. Ambs and Flank⁵⁷ suggested that the thermal stability of synthetic faujasite was dependent only upon the level of sodium present, and that there was no significant difference between decationized Y and ultrastable faujasite. However, Kerr⁵⁸ showed that the high thermal stability produced in a hydrogen-Y zeolite by heating at 973–1073 K (with the chemical water remaining in the environment of the zeolite) corresponded to a situation in which approximately 25% of the aluminium was present in the cationic form. It was also shown that materials of improved thermal stability could be produced by removal of up to 50% of the framework aluminium from a Na-Y zeolite. In a detailed examination of calcination conditions it was demonstrated⁵⁹ that the geometry of the zeolite bed during calcination of the NH_4 -Y zeolite significantly affected the nature of the final product. The ultrastable faujasites were only formed under conditions where the removal of ammonia and water from the bed was impeded.

A detailed X-ray diffraction study⁶⁰ has indicated that the ultrastable Y faujasite has lost 15 framework aluminium atoms per unit cell, and also a significant number of framework oxygen atoms. Jacobs and Uytterhoeven⁶¹ have reported an *i.r.* study of deepbed-calcined NH_4 -Y zeolites, and describe two additional absorption bands at *ca.* 3700 cm^{-1} and 3600 cm^{-1} which appear to be characteristic of ultrastable faujasites. They have assigned these two bands to framework hydroxy-species created during the deepbed calcination procedure, and have suggested that they could correspond to two distinct locations in the framework.

⁵⁶ C. V. McDaniel and P. K. Maher, in 'Molecular Sieves', Society of Chemical Industry, London, 1968, p. 186.

⁵⁷ W. J. Ambs and W. H. Flank, *J. Catalysis*, 1969, **14**, 118.

⁵⁸ G. T. Kerr, *J. Phys. Chem.*, 1967, **71**, 4155; 1968, **72**, 2594.

⁵⁹ G. T. Kerr, *J. Catalysis*, 1969, **15**, 200.

⁶⁰ P. K. Maher, F. D. Hunter, and J. Scherzer, *Adv. Chem. Ser.*, 1971, No. 101, 266.

⁶¹ P. Jacobs and J. B. Uytterhoeven, *J. Catalysis*, 1971, **22**, 193.

Some of the patent literature emphasises the important industrial application of ultrastable faujasites. McDaniel and co-workers claim⁶² that, after heating for two hours at 1173 K, the surface area of stabilized faujasite-type zeolites was only reduced from 870 to 635 m² g⁻¹. Other patents claim^{63–67} that inclusion of an ultrastable component in the zeolite catalyst gives higher hydrocracking and hydrodenitrification activities, with lower fouling rates and a lower starting temperature (for the same conversion) than with conventional zeolite catalysts. The material produced by dealumination of a Y zeolite (to a SiO₂:Al₂O₃ molar ratio of 16.7) has been claimed⁶⁸ to produce a material useful as a support for cracking catalysts.

Beaumont *et al.*^{69,70} have used the cracking of iso-octane (with isobutene as a major product) to examine the catalytic activity of X and Y zeolites exchanged with Ca²⁺ and La³⁺. They also examined the acidity of these materials using Hammett and arylmethanol indicators. Their results indicated that the number of acid sites was dependent upon the valency of the exchanged cation, and that the cracking activity was affected by the nature of the carrier gas (considerably enhanced when hydrogen was used). They concluded that the acidic and catalytic properties were increased when ion exchange took place at the inner cation sites rather than at sites located near or in the supercage. In examining the effect of dealumination (by repeated extraction with edta) they found that the catalytic activity was apparently unaltered until more than 35% of the aluminium was removed from the structure, and they observed three acidity sites of differing strengths.

Moscou^{71,72} has used chemical methods to investigate the acid sites on rare-earth-exchanged (RE) zeolites, *i.e.* by LiAlH₄ reaction and Karl Fischer titration. After heating at 473–573 K the RE-Y zeolites contained only one acidic hydroxy-group, in the supercage, for each rare-earth ion introduced. For a RE-Y zeolite with a SiO₂:Al₂O₃ molar ratio of 5.0, and with 75% of the sodium exchanged by rare-earth cations, the density of acidic hydroxy-groups (Brönsted acid sites) was quoted as 7×10^{20} sites g⁻¹. This value is some 70 times higher than that for amorphous silica-alumina catalysts. Ben Taarit *et al.*⁷³ have also examined the acidic (and oxidizing) properties of rare-earth-exchanged Y zeolites. The i.r. spectrum of RE-Y, after calcination at various temperatures, suggested the presence of both Brönsted- and Lewis-type acidity.

⁶² U.S.P. 3 595 611/1971.

⁶³ U.S.P. 3 535 227/1970.

⁶⁴ U.S.P. 3 536 605/1970.

⁶⁵ U.S.P. 3 536 606/1970.

⁶⁶ U.S.P. 3 558 471/1971.

⁶⁷ G.P. 2 000 026/1970.

⁶⁸ G.P. 2 061 285/1971.

⁶⁹ R. Beaumont and D. Barthomeuf, *Compt. rend.*, 1969, **269**, C, 617; 1971, **272**, C, 363.

⁷⁰ R. Beaumont, D. Barthomeuf, and Y. Trambouze, *Adv. Chem., Ser.*, 1971, No. 102, 327.

⁷¹ L. Moscou and M. Lakeman, *J. Catalysis*, 1970, **16**, 173.

⁷² L. Moscou, *Adv. Chem. Ser.*, 1971, No. 102, 337.

⁷³ Y. Ben Taarit, M. Mathieu, and C. Naccache, *Adv. Chem. Ser.*, 1971, No. 102, 362.

Brief mention has been made of the fact that the cracking patterns observed over Na-X zeolites did not correspond to those observed over typical acidic catalysts. Rabo and Poutsma¹¹ have reported an examination of the cracking of n-hexane and other paraffins over K-Y, Na-Y, and Na,K-exchanged L zeolites at 773 K. The observed product distributions over these alkali-exchanged zeolites could be rationalized in terms of a modified radical mechanism, with double-bond-shift isomerization processes occurring as secondary reactions subsequent to, rather than an inherent part of, the cracking process. It seems clear that with these materials the catalytic activity cannot be associated with ionic-type mechanisms. Miale and Weisz⁷⁴ have reported that the catalytic cracking activity (for n-hexane) of Na-X was increased by a factor of five to ten by contact with H₂S, or S followed by oxygen (air), or with SO₂ alone. In each case the same sulphur-zeolite complex appeared to be formed, the sulphur content corresponding to one sulphur atom for two of the mobile sodium atoms of the aluminosilicate lattice.

The chemistry of the hydrocracking process has been reviewed⁷⁵ with particular reference to the shape selectivity exhibited by zeolites. The use of the small-pore 5A zeolites as shape-selective catalysts was first described by Eng,⁷⁶ and subsequently developed by several authors. Robson *et al.*⁷⁷ have reported the use of synthetic erionite as a selective catalyst for hydrocracking. Tests on a C₅-C₆ naphtha showed strong selectivity for converting n-paraffins to gaseous products, particularly propane. The selectivity decreased, and other components of the naphtha feed were cracked, as the temperature was raised. X-Ray and electron diffraction data indicated that the synthetic erionite used contained intergrowths of the related offretite structure (a relatively large-pore zeolite). Such impurities were believed to be responsible for the manner in which the catalyst exhibited appreciable conversion of branched-chain paraffins which could not enter the erionite pore structure.

Workers at the Mobil laboratories have reported^{27,78} studies on a synthetic offretite containing tetramethylammonium ions (probably located in the large intracrystalline pores along the *c* axis of the offretite lattice). It is claimed⁷⁹ that these materials are good hydrocracking catalysts. Lattice-associated hydroxy-groups, confirmed as protonic in nature by interaction with ammonia, were generated from the tma cations. Dehydroxylation of the acid offretite at about 773 K generated electron-acceptor (Lewis acid) sites. It was noted that higher temperatures were required to convert the NH₄-offretite to the acid form than with NH₄-Y. Vacuum fragmentation of the bulky tma cations within the narrow offretite channels produced a complex product mixture, which could be rationalized, however, by superimposition of a variety of 'classical' reaction patterns.

⁷⁴ J. N. Miale and P. B. Weisz, *J. Catalysis*, 1971, **20**, 288.

⁷⁵ G. E. Langlois and R. F. Sullivan, *Adv. Chem. Ser.*, 1970, No. 97, 38.

⁷⁶ U.S.P. 3 039 953/1962.

⁷⁷ H. E. Robson, G. P. Hamner, and W. F. Arey jun., *Adv. Chem. Ser.*, 1971, No. 102, 417.

⁷⁸ E. L. Wu, T. E. Whyte jun., and P. B. Venuto, *J. Catalysis*, 1971, **21**, 384.

⁷⁹ U.S.P. 3 578 398/1971.

It has also been shown⁸⁰ that thermal decomposition of a series of methylammonium-cation-exchanged Y zeolites will generate protonic sites.

A brief examination of the patent literature indicates that the application of zeolites as catalysts in cracking and hydrocracking processes is still generating a tremendous amount of industrial research. In the past two years some 40 patents additional to those already mentioned have appeared. These reveal the continued interest in the use of rare-earth-exchanged faujasite materials, and also reflect the growing employment of zeolites of the mordenite and erionite type.

Alkylation, Dealkylation, and Isomerization Reactions.—Venuto and co-workers³² have investigated a wide variety of alkylation reactions over zeolite catalysts. They have concluded that such reactions generally proceed *via* carbonium-ion-type mechanisms, and that they showed great similarity to the corresponding features commonly reported for electrophilic aromatic substitution in the presence of strong protonic acids, such as concentrated H_2SO_4 , liquid HF, or promoted Lewis acids. Normally *ortho,para*-orientation was observed, and selectivity for attack on the reactive (nucleophilic) aromatic nucleus was exhibited in competitive situations. They based their conclusions about the nature of the reaction on an analysis of the structures of the alkylaromatic products, the patterns of substrate reactivity, and the pathways of side-reactions. Their results provided qualitative evidence for a Rideal-like mechanism where in an olefin alkylation the initial step would be the fast, reversible, non-competitive adsorption of the olefin on the catalyst acidic sites.

Mays and Pickert⁸¹ reported that multivalent-cation-exchanged and decationized Y zeolites were excellent catalysts for the alkylation of aromatic hydrocarbons with C_2 – C_{12} olefins or alkyl halides. High reaction rates were obtained at low temperatures and pressures with high selectivities. The observed activity was comparable to that of aluminium chloride promoted by HCl, and considerably higher than that exhibited by amorphous silica–alumina or supported (or non-supported) mineral acids. The zeolites would alkylate with good selectivity and give high yields with species such as thiophen or phenolic ethers, which would be readily degraded by mineral acids.

Pickert *et al.*⁸² observed that the alkylation activity of faujasite catalysts (for the benzene–propene alkylation reaction) was enhanced with increase in calcination temperature. The condition for maximum activity corresponded to the situation where all the residual hydroxy-groups associated with catalytically-active sites had been removed. It was suggested that the carbonium ion intermediates were formed by polarization of the reactant hydrocarbons (by the electrostatic fields set up by the cations). However, Rabo *et al.*⁸³ reported that

⁸⁰ E. L. Wu, G. H. Kuhl, T. E. Whyte jun., and P. B. Venuto, *Adv. Chem. Ser.*, 1971, No. 101, 490.

⁸¹ R. L. Mays and P. E. Pickert, in 'Molecular Sieves', Society of Chemical Industry, London, 1968, p. 112.

⁸² P. E. Pickert, A. P. Bolton, and M. A. Lanewala, presented at the 59th American Institute of Chemical Engineers Meeting, Columbus, Ohio, 1966.

⁸³ J. A. Rabo, C. L. Angell, and V. Schomaker, in 'Proceedings of the 4th International Congress on Catalysis', Moscow, 1968, vol. 3, p. 966.

the activity of a La-Y zeolite (for the toluene-propene alkylation reaction) was not affected by changes in the calcination temperature. The La-Y showed high activity at room temperature whether activated at 823 K or near 973 K. It was postulated that oxygen-deficient lattice sites (Lewis acid sites) generated during the 973 K activation could have alkylation activity. More recently, Morita and co-workers,⁸⁴ in a study of the alkylation activity (for benzene-ethylene alkylation) of La-Y reported a decrease in activity with increase in catalyst-pretreatment temperature (over the range 448–548 K). They suggested the catalyst was being poisoned by adsorption of excess water on the active sites.

Recent patents have claimed that the H-Y zeolite is a good catalyst for benzene alkylation with propane,⁸⁵ and that Y zeolites containing rare-earth, manganese, or aluminium ions are good alkylation catalysts for the preparation of C₈ hydrocarbons from isobutane and but-1-ene.⁸⁶ Isakov *et al.*⁸⁷ have reported that benzene alkylation (with propene) proceeds rapidly on Y zeolites exchanged with Ca²⁺ or Cd²⁺. An increase in activity with increase in extent of ion exchange was observed.

An examination⁸⁸ of the alkylation activity of toluene with methanol for a series of Y zeolites has found the following relative order of activity: RE-Y > H-Y > bivalent forms > univalent forms. Selective formation of *p*-xylene in the product mixture was noted, *e.g.* in excess of 50%, compared to the thermodynamic equilibrium quantity of about 22%. The authors suggested that depression of the secondary isomerization reaction of the initially-formed xylene in the zeolite supercages was responsible for such selectivity. Addition of HCl to a Mn-Y zeolite promoted the *p*-xylene selectivity, presumably suggesting a correlation with Brønsted acidity. There was also a correlation between the extent of cation exchange and the catalytic activity (and the *p*-xylene selectivity).

Sidorenko and Galich⁸⁹ have also investigated the mechanism of toluene methylation over zeolite catalysts. For Na-alkaline-earth zeolites they noted that Y zeolites were more active than X zeolites, and the activity decreased from magnesium to strontium. They postulated a mechanism involving the decomposition of protonated methanol (the essential first step) to methylene radicals and H₃O⁺ acid sites on the catalyst. The absence of either ethylbenzene or styrene was attributed to the specific geometry of adsorption of the toluene, which prevented insertion of the methylene radical into the C–H bonds of the side chain. Kawakami *et al.*⁹⁰ have stated that alkali-metal Y zeolites are active for methyl migration of anisole in the temperature range 598–723 K, and they reported relative activities in the order Li-Y > Na-Y > K-Y > Rb-Y. The rates

⁸⁴ Y. Morita, M. Takayasu, and H. Matsumoto, *Kogyo Kagaku Zasshi*, 1970, **73**, 2540.

⁸⁵ G.P. 1 934 426/1970.

⁸⁶ G.P. 1 931 425/1970.

⁸⁷ Y. I. Isakov, N. V. Mirzabekova, V. I. Bogomolov, and Kh. M. Minachev, *Neftekhimiya*, 1970, **10**, 520.

⁸⁸ T. Yashima, K. Yamazaki, H. Aymad, M. Katsuta, and N. Hara, *J. Catalysis*, 1970, **16**, 273; **17**, 151.

⁸⁹ Y. N. Sidorenko and P. N. Galich, *Ukrain khim. Zhur.*, 1970, **36**, 1234.

⁹⁰ S. Kawakami, S. Takanashi, and S. Fujii, *Kogyo Kagaku Zasshi*, 1971, **74**, 899.

of formation of phenol, cresol, and methylanisole, together with the rate of conversion of anisole, were all zero order with respect to anisole.

The zeolites that catalyse alkylation processes will also act, in general, as catalysts for dealkylation, and patent claims invariably link together alkylation and dealkylation activity. However, it is evident⁷ that considerably higher temperatures are normally required for dealkylation. The cumene-dealkylation reaction discussed in the previous section is probably the most widely studied example of this type. A recent patent⁹¹ refers to the use of a modified mordenite catalyst for the selective dealkylation of C_8+ hydrocarbons, with the selective nature of the catalyst being a function of the mordenite pore structure.

A large number of papers have been published concerned with the catalytic activity of zeolites for the transalkylation and isomerization of alkyl-aromatic species. In the very thorough investigation of the relationship between catalytic activity and zeolite structural properties, Ward³⁹ correlated his i.r. data with *o*-xylene isomerization activity. Attention has recently been focussed upon the activity of alkaline-earth Y zeolites,^{92,93} where NH_4 -Y has been back-exchanged with Ca^{2+} and Mg^{2+} . The changes in activity observed as the extent of exchange was altered have been correlated with accessible acid site concentrations, and ascribed to the different polarizing effects of the two cations on the site strength. The observed increase in catalytic activity was matched by an increase in the Brönsted acid site concentration, with the Mg-Y zeolites being more acidic than Ca-Y. The Brönsted acidity, and the *o*-xylene isomerization activity, was also reported to increase with increase in the $SiO_2:Al_2O_3$ molar ratio. Sidorenko and Galich⁹⁴ have also reported that zeolites containing alkaline-earth metals are more active for *m*-xylene rearrangements than those containing alkali metals. They attributed their results to the greater acidity of water molecules associated with the polyvalent ions.

Bolton *et al.*⁹⁵ proposed that the isomerization of diethyl-benzenes over a modified Y zeolite occurred *via* a transalkylation mechanism involving diphenylethane-type intermediates. However, such a mechanism cannot occur unless readily-extractable α -hydrogen atoms are available, *i.e.* not if the alkyl group is *t*-butyl. Csicsery and Hickson⁹⁶ examined the isomerization of 2-ethyl-1-methylbenzene over a series of Y zeolites (in the temperature range 473–673 K). They found that two major independent reactions were taking place, *i.e.* isomerization to 3-ethyl-1-methylbenzene and 4-ethyl-1-methylbenzene, and transethylation to toluene and diethylmethylbenzenes. For a given catalyst the isomerization:transethylation ratio increased with increasing water content of the reaction mixture. They concluded that their results could be explained if the isomerization process was primarily catalysed by Brönsted acid sites, whereas the transethylation was primarily a Lewis acid-catalysed reaction; or if the transethylation was

⁹¹ Fr.P. 2 010 151/1970.

⁹² J. W. Ward, *J. Catalysis*, 1970, **17**, 355.

⁹³ R. C. Hansford and J. W. Ward, *Adv. Chem. Ser.*, 1971, No. 102, 354.

⁹⁴ Y. N. Sidorenko and P. N. Galich, *Ukrain. khim. Zhur.*, 1970, **36**, 1120.

⁹⁵ A. P. Bolton, M. A. Lanewala, and P. E. Pickert, *J. Org. Chem.*, 1968, **33**, 1513.

⁹⁶ S. M. Csicsery and D. A. Hickson, *J. Catalysis*, 1970, **19**, 386.

catalysed by a Brönsted–Lewis site-pair, and the isomerization was catalysed by a single-type Brönsted acid site.

Csicsery⁹⁷ has examined the shape-selectivity exhibited by mordenite for transalkylation processes. Symmetrical trialkylbenzenes are normally the predominant components of trialkylbenzene isomer mixtures at thermodynamic equilibrium. However, although mordenite catalysts have adequate isomerizational activity, no symmetrical isomers are formed (in marked contrast to the product distribution observed over X and Y zeolites). There is thus shape-selective kinetic control where the special crystal structure of the catalyst prevents the formation of the thermodynamically favoured isomer. The effective channel diameters in acid mordenite are between the minimum cross-sections of the wider symmetrical trialkylbenzenes and the other trialkylbenzene species (approximately 0.86 and 0.82 nm, respectively). It was noted that the mordenite catalysts were deactivated much faster than the Y zeolites, presumably because the mordenite pore system can be more easily blocked by strongly adsorbed molecules.

The importance for transalkylation reactions of aromatic species of catalysts based on the mordenite structure is demonstrated by several patents^{98–101} where either the acid form or nickel-containing mordenites are claimed to be active for such processes at attractively low temperatures. Japanese workers¹⁰² reported that H-mordenite was an effective catalyst for the disproportionation of toluene, but that bivalent cation-exchanged synthetic mordenites exhibited little activity for this reaction.

There have been a number of reports of the manner in which multivalent metal cation and decationized Y zeolites (usually containing small amounts of a noble metal) exhibit high activity and selectivity for the isomerization of C₄–C₆ n-paraffins. Penchev *et al.*¹⁰³ have compared the acidity and catalytic activity (for the isomerization of n-hexane and cyclohexane) of Ca-Y, Mg-Y, and a Y zeolite containing Pt. They noted that the acidity (and activity) increased with Ca²⁺ and Mg²⁺ content, but that the Pt content did not apparently affect the zeolite acidity. Kubasov *et al.*¹⁰⁴ also examined cyclohexene isomerization over a series of Y zeolites, and reported that the activity fell in the order L-Y > H-Y > Ca-Y. Maximum isomerization was noted just before the onset of cracking, and the formation of cyclohexane (evidently by a parallel reaction on different active centres) also took place. They were not able to establish any correlation of the catalytic activity with a particular acidity type, and suggested that the conversion occurred on both types of active centres by different

⁹⁷ S. M. Csicsery, *J. Catalysis*, 1970, **19**, 394; 1971, **23**, 124.

⁹⁸ G.P. 1 925 102/1970.

⁹⁹ G.P. 1 946 187/1970.

¹⁰⁰ G.P. 2 000 491/1971.

¹⁰¹ G.P. 2 006 902/1971.

¹⁰² T. Yashima, H. Moslehi, and N. Hara, *Bull. Japan Petrol. Inst.*, 1970, **12**, 106.

¹⁰³ V. Penchev, V. Kanazirev, and Khr. Minchev, *Compt. rend. Acad. bulg. Sci.*, 1969, **22**, 899.

¹⁰⁴ A. A. Kubasov, A. N. Ratov, K. V. Topchieva, and L. M. Vishnevskaya, *Vestnik Moskov. Univ.*, 1970, **11**, 406.

mechanisms. A recent article¹⁰⁵ describes the hydroisomerization process operated by Shell, where C_5 and C_6 paraffins are converted, in the vapour phase, over zeolites containing noble metal, into highly-branched compounds with high octane numbers.

Beecher and Voorhies¹⁰⁶ showed that a synthetic H-mordenite catalyst had a high n-hexane isomerization activity, with or without dispersed noble metal. The effect of pressure on the rate constant for the isomerization process was consistent with a dual-site catalytic mechanism. The hydroisomerization of cyclohexane (to methylcyclopentane) has also been reported^{107,108} to provide data consistent with a dual-site mechanism over a series of H-mordenite catalysts containing Pd, and with differing $SiO_2:Al_2O_3$ molar ratios. The activation energies for the isomerization were similar to those for large-pore zeolites, so it was concluded that there were no macropore diffusion limitations to the results. Cyclohexane isomerization has been examined,¹⁰⁹ over Pt- Al_2O_3 -mordenite catalysts, and it was found that simultaneous isomerization and dehydrogenation occurred with significant diffusional effects. Ammonia-chemisorption experiments suggested that the mordenite component of the catalyst was some twelve times more acidic than the alumina, and the isomerization activity was reported to be directly related to the catalyst acidity.

Minachev *et al.*¹¹⁰ have also examined the catalytic isomerization properties (for cyclohexane and n-pentane) of synthetic mordenites. They reported that H-mordenite was more active than bivalent and trivalent cation-exchanged forms, and that the Na-, Li-, and K-exchanged mordenites had negligible isomerization activity. They postulated that the mechanism over H-mordenite was different to that normally attributed to metal-zeolite isomerization catalysts. It was suggested that the carbonium ion species was formed by the splitting off of a hydride ion from the saturated molecule of the starting hydrocarbon, and not *via* the attachment of a proton. Eberly *et al.*¹¹¹ have investigated the dealumination of a series of acid mordenite samples (containing 0.5% by weight Pd) with particular regard to the effect upon acidity and catalytic activity for n-pentane hydroisomerization; $SiO_2:Al_2O_3$ ratios from 12–97 were prepared. I.r. spectral changes, together with ammonia-adsorption data, indicated that the surface acidity was decreasing with increase in the $SiO_2:Al_2O_3$ ratio. As the catalytic activity also decreased, it was concluded that the surface acidity was the dominant factor in the process.

The isomerization of cyclopropane over Na-Y and NH_4 -Y has been correlated¹¹² with the Brønsted acidity of the zeolites. The nature of the deuteriated

¹⁰⁵ H. W. Kouwenhoven and W. C. Van Zijll Langhout, *Chem. Eng. Progr.*, 1971, **67**, 65.

¹⁰⁶ R. Beecher and A. Voorhies, *Ind. and Eng. Chem. (Product Res. and Development)*, 1969, **8**, 366.

¹⁰⁷ J. R. Hopper, *Diss. Abs. (B)*, 1970, **30**, 5026.

¹⁰⁸ A. Voorhies and J. R. Hopper, *Adv. Chem. Ser.*, 1971, No. 102, 410.

¹⁰⁹ D. E. Allan, *Diss. Abs. (B)*, 1971, **31**, 4652.

¹¹⁰ Kh. Minachev, V. Garanin, T. Isakova, V. Kharlamov, and V. Bogomolov, *Adv. Chem. Ser.*, 1971, No. 102, 441.

¹¹¹ P. Eberly, C. N. Kimberlin, and A. Voorhies, *J. Catalysis*, 1971, **22**, 419.

¹¹² Z. M. George and H. W. Habgood, *J. Phys. Chem.*, 1970, **74**, 1502.

propene species obtained when the isomerization was carried out over a completely deuteriated catalyst suggested that the cyclic $C_3H_6D^+$ ion was able to equilibrate with the various isotopic forms before ring-opening occurred. Flockhart *et al.*¹¹³ have considered the effect of calcination temperature upon the cyclopropane isomerization activity of a Na-Y zeolite partially exchanged with NH_4^+ . They also found a clear correlation between Brønsted acidity and activity, but a second mechanism appeared to be operative at high calcination temperatures (*ca.* 930 K) where the Brønsted acidity was low. Under such conditions the electron-donor power, as measured by the formation of trinitrobenzene anion radicals from the adsorbed parent molecule, was at a maximum. It was therefore postulated that the active site could be either a Lewis acid centre or possibly an electron-transfer site of the type responsible for the redox activity of zeolites.

The isomerization of n-butenes, without skeletal rearrangement, has received considerable attention as a test reaction for the characterization of zeolite catalysts. Dimitrov and Leach¹¹⁴ found that Na-X was relatively inactive (requiring temperatures above 475 K), but a marked increase in activity was observed on exchange with Cu^{2+} cations. The initial *cis-trans* but-2-ene product distribution over Na-X, and the low-exchanged Cu-X, was compatible with a radical-type mechanism. Cross *et al.*^{115,116} have reported a range of initial product ratios for a series of cation-exchanged X zeolites. Results with Ce-X (and the majority of other zeolites examined) were indicative of a carbonium ion mechanism. Over Ni-X, and to a lesser extent Zn-X, however, a radical-type mechanism was proposed. Evidence in support of this was obtained by following the isomerization in the presence of (i) deuterium (when an enhancement of rate and extensive exchange were observed), or (ii) deuterium oxide (when very little exchange occurred and the reaction rate was virtually unchanged). Tempere and co-workers¹¹⁷ have reported *cis:trans* product ratios of *ca.* 2.0 for the but-1-ene isomerization over a series of X and Y zeolites, but over an A-type zeolite reported that *trans*-but-2-ene was the major product. They concluded that the active sites for the isomerization were hydroxy-groups localized in hexagonal sites (corresponding to an i.r. absorption band at 3600 cm^{-1}), and that the activity was not directly dependent upon the electrostatic field of the exchanged cation.

Hall *et al.*¹¹⁸ have examined the manner in which the activity and selectivity (for the but-1-ene isomerization) of an Na-Y zeolite were modified by exchanging small amounts of Ca^{2+} and by creation of a cation deficiency by hydrolysis. As the Ca^{2+} content (and the acidity) was increased, *cis-trans* isomerization was enhanced relative to double-bond migration, and it was also reported that the

¹¹³ B. D. Flockhart, L. McLoughlin, and R. C. Pink, *Chem. Comm.*, 1970, 818.

¹¹⁴ Chr. Dimitrov and H. F. Leach, *J. Catalysis*, 1969, **14**, 336.

¹¹⁵ N. E. Cross, C. Kemball, and H. F. Leach, *Adv. Chem. Ser.*, 1971, No. 102, 389.

¹¹⁶ N. E. Cross, C. Kemball, and H. F. Leach, *J. Chem. Soc. (A)*, 1971, 3315.

¹¹⁷ J. F. Tempere, J. Kermarec, and B. Imelik, *Bull. Soc. chim. France*, 1970, 3808, 4227.

¹¹⁸ W. K. Hall, E. A. Lombardo, and G. A. Sill, *J. Catalysis*, 1971, **22**, 54.

catalytic activity increased with increasing cation deficiency (up to 0.94% original Na^+ extracted by hydrolysis). From data obtained using added water as a co-catalyst, it was concluded that the reaction intermediate was the *s*-butyl carbonium ion. Furthermore, it was postulated that a pure alkali-Y zeolite containing no cation deficiency, no bivalent ions, and therefore no decationized sites, would have negligible catalytic activity for the isomerization of *n*-butenes.

Oxidation Reactions.—Crystalline aluminosilicates show very little intrinsic catalytic activity for oxidation reactions, and oxidation processes over zeolites invariably feature materials containing transition-metal ions, *e.g.* Mn-Y has been reported⁷ to catalyse the oxidative dehydrogenation of ethylbenzene to styrene and the selective oxidation of benzyl alcohol to benzaldehyde in the temperature range 523–643 K. Fripiat and co-workers^{119–121} reported the liquid-phase oxidation of several hydrocarbon species by X zeolites containing Co, Mn, or Mo. In the oxidation of *p*-xylene over a mixed Co–Mn–X zeolite they observed high selectivity for terephthalic acid formation, and over Mo–X propene was selectively oxidized to propene oxide. It was postulated that the high oxidation activity exhibited was related to the promotion of electron-unpairing in the transition-metal cations by the zeolite support.

The series of papers by Mochida *et al.*¹²² is concerned with catalytic oxidation of propene and ethylene over Y zeolites containing transition-metal cations. They noted that the oxidation of propene over Cu–Y, in the presence of steam, exhibited some selectivity, with the preferential formation of acrolein. The relative order of oxidation activity was given as $\text{Pd} \approx \text{Pt} > \text{Cu} > \text{Tl} > \text{Ag} > \text{Mn} > \text{Ni} > \text{Co} > \text{Zn} > \text{V} > \text{Cr} > \text{Na}$. The reaction orders were all observed to be approximately 0.5 in oxygen over the various zeolites, but to vary for propene. It was therefore concluded that the olefin adsorption was important in the oxidation process, and the activity sequence was correlated with a parameter expressing the tendency of the metal cation to form a dative π -bond. Iron-containing zeolites have also been reported¹²³ to exhibit good catalytic activity for propene oxidation.

Van Sickle and Prest¹²⁴ have examined the reaction of oxygen with cyclopentene, but-1-ene, and but-2-ene adsorbed on cobalt-exchanged A and X zeolites in the temperature range 298–363 K. They reported oxidation rates some 500–600 times greater than in more conventional homogeneous oxidation systems. However, there were a multiplicity of products, many of which were tightly bound to the zeolites (especially the A-type zeolites). The products were also different in structure: the principal products of homogeneous oxidations are hydroperoxides, but the more prominent volatile products from the butene

¹¹⁹ J. Rouchaud, L. Sondengam, and J. J. Fripiat, *Bull. Soc. chim. France*, 1968, 4387.

¹²⁰ J. Rouchaud, P. Mulkay, and J. J. Fripiat, *Bull. Soc. chim. belges*, 1968, 77, 537.

¹²¹ J. Rouchaud and J. J. Fripiat, *Bull. Soc. chim. France*, 1969, 78.

¹²² I. Mochida, S. Hayata, A. Kato, and T. Seiyama, *J. Catalysis*, 1969, **15**, 314; 1970, **19**, 405; 1971, **23**, 31.

¹²³ L. V. Skalkina, I. K. Kolchin, E. Y. Margolis, N. F. Ermolenko, S. A. Levina, and L. N. Melashevich, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1970, 980.

¹²⁴ D. E. Van Sickle and M. L. Prest, *J. Catalysis*, 1970, **19**, 209.

oxidation over zeolites were methyl ethyl ketone, crotonaldehyde, and but-2-ene-1-ol.

In an e.s.r. investigation of cationic oxidation sites in faujasite, Richardson¹²⁵ suggested that an electron-transfer process took place at the Cu^{2+} ion in Cu-Y zeolites containing 2% by weight of Cu. Naccache and Ben Taarit¹²⁶ have further examined the oxidizing (and acidic) properties of Cu-Y, using e.s.r. and i.r. spectroscopic techniques. They found that at low activation temperatures the zeolite exhibited Brønsted acidity and no true Lewis acid sites could be detected. However, carbon monoxide treatment of the zeolites caused reduction (cupric to cuprous) and formed Lewis acid centres. They concluded that the oxidizing properties of the cupric Y zeolite could be attributed to the cupric ions, whereas those of the reduced samples were due to the true Lewis acid sites.

Miscellaneous Catalytic Studies.—In this section a limited number of further points of catalytic significance, which in themselves do not justify separate sections, will be discussed.

In the paper⁷⁴ in which the cracking activity of Na-X was reported to be increased by the inclusion of sulphur, it was also noted that the catalytic activity was increased by the inclusion of selenium or tellurium. However, the catalyst then became a dehydrocyclization catalyst rather than a cracking catalyst. Further communications^{127,128} from the Mobil laboratories have reported a more detailed examination of this novel dehydrocyclization catalyst, particularly the catalyst containing tellurium. The test reaction for this activity was the aromatization of n-hexane (to benzene). X-Ray examination indicated the presence of tellurium, both within the sodalite cage and within the supercage. It was established that the presence of a significant concentration of cations in type III sites was essential for the catalytic activity, and it was postulated that the catalytically-active entity was a tellurium ion situated in the zeolite supercage and co-ordinated to cations in type II and type III sites.

It is generally considered that, for the majority of situations, catalysis over zeolites occurs within the zeolite porous structure. In shape-selective catalysis the situation corresponds to molecules of suitable dimensions continuously entering and leaving the molecular sieve cavities. The situation of reactant selectivity corresponds to the case where only one of two classes of reactant molecules can pass through the pores; on the other hand, with product selectivity only those products (formed within the porous structure) with suitable dimensions can diffuse out and appear as observed products. However, there are clearly many instances where reactions which cannot occur within the zeolite have been reported, e.g. the formation of acetophenone tetramer over H-Y,¹⁰ and in such circumstances the external surface must play some catalytic role. Differences in reactivity, and selectivity, of such surface sites could be expected as the environment

¹²⁵ J. T. Richardson, *J. Catalysis*, 1967, **9**, 172.

¹²⁶ C. Naccache and Y. Ben Taarit, *J. Catalysis*, 1971, **22**, 171.

¹²⁷ W. H. Lang, R. J. Mikovsky, and A. J. Silvestri, *J. Catalysis*, 1971, **20**, 293.

¹²⁸ R. J. Mikovsky, A. J. Silvestri, E. Dempsey, and D. H. Olson, *J. Catalysis*, 1971, **22**, 371.

of the reactant molecules would be totally different and no diffusion restrictions would be applicable. Such surface (external) reactions could reduce the selectivity of the zeolite catalyst and, in fact, enhanced selectivity has recently been claimed¹²⁹ by reduction of the catalytic activity of the external surface. An erionite zeolite containing nickel, when treated with copper acetate, was reported to have negligible undesirable side-reactions (presumably on the external surface between molecules unable to enter the pore structure), e.g. isoparaffin formation from 2-methylpentane hydrocracking. A similar improvement in selectivity has been disclosed¹³⁰ by poisoning of the external sites with a large, organic, phosphorus-containing compound such as tricresyl phosphate.

Thomas and Barmby¹³¹ proposed that the primary cracking of gas oil molecules on zeolite catalysts occurred on the external surface of the catalysts. They considered that the improved gasoline products obtained, relative to those obtained over amorphous silica-alumina materials, resulted from subsequent hydrogen-transfer reactions of the gasoline species within the zeolitic structure. However, Weisz⁴ has suggested that the unusually high k_h/k_c ratio for the interior of the zeolite, where k_h refers to hydrogen transfer and k_c to cracking, is sufficient to account for the unusual product distributions of the zeolites, and that participation of the external surface is not substantial.

It has already been noted that mordenite zeolites, particularly the H form, are active alkylation catalysts, e.g. for alkylation of benzene with propene. In this context the studies of Satterfield and co-workers concerning the diffusion of hydrocarbon species within mordenite systems are very relevant. The rates of diffusion of methane, butane, isobutane, and perfluorobutane were observed¹³² to exhibit a maximum with time in single crystals of Na-mordenite, in the temperature range 298–373 K. A more detailed examination of the diffusion properties of benzene and cumene in H-mordenite¹³³ indicated that counter-diffusion of these species was very small (relative to the situation in Y zeolites). Observed changes in the desorptive diffusion coefficient of cumene were attributed to the slow formation, in the H-mordenite pores, of large molecular species *via* cumene disproportionation which blocked the pores. It was concluded that the major portion of the internal area of H-mordenite was apparently unavailable for reaction of aromatic species at temperatures moderately above ambient. The suggestion was made that the alkylation-type reactions must occur either on the external surface or just within the pore mouth. Venuto¹⁰ has also postulated pore-mouth catalysis to explain the relative isomerization and deuteration rates of 2,3-dimethylbut-1-ene over a deuteriated Y zeolite. It was there suggested that the limited extent of deuteration corresponded to a situation in which the majority of the intracrystalline OD groups were effectively inaccessible, and that

¹²⁹ U.S.P. 3 554 900/1971.

¹³⁰ U.S.P. 3 575 845/1971.

¹³¹ C. L. Thomas and D. S. Barmby, *J. Catalysis*, 1968, **12**, 341.

¹³² C. N. Satterfield and W. G. Margetts, *Amer. Inst. Chem. Engineers J.*, 1971, **17**, 295.

¹³³ C. N. Satterfield, J. R. Katzer, and W. R. Vieth, *Ind. and Eng. Chem. (Fundamentals)*, 1971, **10**, 478.

only those species near to the external surface were operative in the exchange (deuteriation) reaction.

Although the majority of reactions catalysed by zeolites have been shown to occur as a result of the acidic nature of the catalysts, mention has already been made of particular instances where radical-type reactions are observed, and intermediates of a non-ionic character have been postulated. A paper by Venuto and Landis,¹³⁴ in which the formation of stilbenes from reactions of benzyl-type mercaptans was examined, gives an example where the presence of the zeolite alters the reaction very considerably (both in terms of increased activity and stilbene selectivity) but not as a direct consequence of the acidity of the zeolite. It has been suggested that in this particular instance the enhanced activity can possibly be explained in terms of the large surface area and a concentration (of reactant) effect rather than the more-specific catalyst interactions normally invoked to rationalize the catalytic activity of zeolites.

The redox activity of zeolites was briefly mentioned in connection with the isomerization of cyclopropane, and Roginskii *et al.*¹³⁵ have further examined the redox activity of a series of transition-metal-exchanged Y zeolites. They reported that in all cases there was enhanced catalytic activity, relative to Na-Y, for the oxidation of hydrogen, carbon monoxide, ethylene, and ammonia. They concluded that the active centres were closely associated with the transition-metal cations. Minachev⁹ has also discussed the redox catalytic activity of zeolites and noted that, in such reactions, zeolites with a lower $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio, and hence a higher cation density, are generally more active. This is in marked contrast to reactions in which carbonium ions are involved. Although possibly not a redox reaction, the high activity of Na-mordenite for the hydrogenation of benzene (in the absence of any conventional hydrogenating components such as Pt, Pd, or Ni), reported by Minachev *et al.*,¹¹⁰ appears to be a particularly important reaction in this context. The hydrogenation activity decreased sharply when Na^+ was replaced by H^+ , and could be generated by treatment of H-mordenite with sodium chloride, so the direct participation of sodium cations in the benzene hydrogenation seems well established.

The major role played by i.r. spectroscopy and X-ray diffraction techniques in the characterization of zeolite catalysts has already been indicated. It is instructive to briefly consider some of the other techniques that are now being employed to obtain information about zeolites. Calorimetric studies, both heats of adsorption¹³⁶ and heats of immersion,¹³⁷ have recently been reported where the data have been used (i) to measure the acidity of sites in X zeolites, and (ii) to suggest that the electrostatic field is the source of the catalytically-active site for carbonium ion reactions of Ca-Y zeolites. In an examination of the nature of rare-earth-exchanged Y zeolites, Bolton¹³⁸ has combined i.r. studies with thermo-

¹³⁴ P. B. Venuto and P. S. Landis, *J. Catalysis*, 1971, **21**, 330.

¹³⁵ S. Z. Roginskii, O. V. Al'tshuler, O. M. Vinogradova, V. A. Seleznev, and I. L. Tsitovskaya, *Doklady Akad. Nauk S.S.S.R.*, 1971, **196**, 872.

¹³⁶ Y. Okamoto, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Japan*, 1970, **43**, 3353.

¹³⁷ K. Tsutsumi and H. Takahashi, *J. Phys. Chem.*, 1970, **74**, 2710.

¹³⁸ A. P. Bolton, *J. Catalysis*, 1971, **22**, 9.

gravimetric analysis. The latter technique indicated that, stoichiometrically, one water molecule was associated with each rare-earth cation. Tung¹³⁹ has proposed the concept of dynamic Brønsted acidity, *i.e.* variation of acid strength with time, to explain aspects of the activity of zeolites. This proposal arose out of his measurements of the dielectric response to temperature and electrical frequency changes, which indicated considerable ionic movement over the zeolite surface.

Dyer *et al.*¹⁴⁰ have observed the mobility of Sr^{2+} and Ba^{2+} cations in X zeolites using radiochemical techniques, and Gallezot and co-workers¹⁴¹ have reported an X-ray study of the movement of copper cations in Y zeolites after ammonia or pyridine chemisorption. They observed some displacement of Cu^{2+} from I sites to I' sites after ammonia treatment, and a more substantial migration of Cu^{2+} into the zeolite supercages (from I and I' sites) subsequent to pyridine adsorption. Naccache and Ben Taarit¹⁴² have interpreted changes in the e.s.r. spectrum of Cu-Y zeolites after treatment with water, ammonia, or pyridine in terms of a similar migration of the cupric ions. Mikkeiken *et al.*¹⁴³ have also reported an e.s.r. (and optical) spectroscopic study of the localization of Cu^{2+} in Y zeolites. They concluded that the cations were initially adsorbed as octahedral aquo-complexes. On dehydration the symmetry decreased and, after treatment at 773 K *in vacuo*, the Cu^{2+} became stabilized in hexagonal sites of the sodalite cages. Leith and co-workers¹⁴⁴ employed e.s.r. techniques in an investigation of the nature of Cu-X zeolites. The spectra suggested the presence of exchanged cations in more than one crystallographic environment. It was shown that the Cu^{2+} in one particular environment reacted preferentially with but-1-ene at temperatures where the Cu-X zeolites were active for n-butene isomerization.

Following the early work of Stamires and Turkevich¹⁴⁵ there have been an extensive number of reports on the application of e.s.r. techniques to the study of the generation of free-radical species on zeolites. Papers describing the formation of biphenyl cation radicals from benzene over an ammonium-mordenite catalyst,¹⁴⁶ and the e.s.r. spectra arising from the adsorption of olefins on RE-Y zeolites¹⁴⁷ typify such studies. In an investigation of the properties of lanthanide-exchanged zeolites, Neikam¹⁴⁸ used e.s.r. data to show that the high radigenic activity of cerium-exchanged zeolites (relative to other lanthanide-exchanged zeolites) resulted from the presence of Ce^{4+} , which was formed during activation in the presence of oxygen.

¹³⁹ S. E. Tung, *J. Catalysis*, 1970, **17**, 24.

¹⁴⁰ A. Dyer, R. B. Gettins, and R. P. Townsend, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2395.

¹⁴¹ P. Gallezot, Y. Ben Taarit, and B. Imelik, *Compt. rend.*, 1971, **272**, C, 261.

¹⁴² C. Naccache and Y. Ben Taarit, *Chem. Phys. Letters*, 1971, **11**, 11.

¹⁴³ I. Mikheiken, V. A. Shvets, and V. B. Kazanskii, *Kinetika i Kataliz*, 1970, **11**, 747.

¹⁴⁴ I. R. Leith, C. Kemball, and H. F. Leach, *Chem. Comm.*, 1971, 407.

¹⁴⁵ D. N. Stamires and J. Turkevich, *J. Amer. Chem. Soc.*, 1964, **86**, 749.

¹⁴⁶ Y. Kuita, T. Sonoda, and M. Sato, *J. Catalysis*, 1970, **19**, 82.

¹⁴⁷ G. Raseev, *J. Catalysis*, 1971, **20**, 120.

¹⁴⁸ W. C. Neikam, *J. Catalysis*, 1971, **21**, 102.

Stevenson¹⁴⁹ has indicated how a detailed examination of the lineshape of the ^1H n.m.r. spectrum of an H-Y zeolite can be analysed to provide data concerning the precise location of protons in the zeolitic framework. Freude *et al.*¹⁵⁰ have also analysed the n.m.r. lineshape of a decationized Y zeolite, and concluded that the hydroxy-groups existed mainly in pairs with an inner proton-proton distance of 0.37 nm. Such an analysis requires the modification of what is a rather sophisticated model in the first instance; consequently the technique has not yet been widely employed. However, such work is an indication of the sophisticated and detailed data concerning the structure of zeolite catalysts that one might expect to be available in the future.

¹⁴⁹ R. L. Stevenson, *J. Catalysis*, 1971, **21**, 113.

¹⁵⁰ D. Freude, D. Mueller, and H. Schmiedel, *Surface Sci.*, 1971, **25**, 289.