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# APPLICATION OF SYNTHETIC ZEOLITES (MOLECULAR SIEVES) TO CATALYSIS

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## I. INTRODUCTION

Natural crystalline aluminosilicates (zeolites, molecular sieves) were shown in 1915 to have catalytic properties.

Catalysts for cracking, oxidation, and other reactions (both inorganic and organic), based on these materials, were subsequently patented[1], but initially they did not find wide practical use.

Advances in the field of zeolite synthesis, mainly in the period 1940–1950, have revealed new potentialities for these materials. Dozens of zeolites with enhanced adsorption properties and thermal stability were prepared, including some which have no natural counterpart. The production of types A and X synthetic zeolites on a semi-industrial scale[2] began in 1954: since then, these zeolites have achieved wide popularity as sorbents for drying, purification, and separation[3,4]. However, their catalytic properties have been very little studied[5], in spite of their great potential importance, which arises from the striking specificity of their properties, making possible the solution of many practical and theoretical problems in catalysis. The combination of a well-defined crystalline structure with uniform pores of molecular dimensions enables highly selective catalysts to be prepared[6–8]. By using zeolites with orifices (leading to voids within the crystals) of the correct size, we can localise reactions on the outer surface of the catalyst and eliminate the influence of internal diffusion. The aluminium in crystalline alumina–silica zeolites always has tetrahedral coordination. (This applies to the cationic forms: three-coordinated aluminium is also present in decationated modifications.) The excess negative charge of the aluminium–silicon–oxygen skeleton is compensated by cations of different elements (when first synthesised, zeolites are usually in the sodium form). These cations can be exchanged for equivalent amounts of other cations, giving rise to various ion-exchanged modifications with a range of different catalytic properties. Multifunctional multicomponent catalysts, obtained by introducing various catalytically active components into the voids of zeolites, have enhanced stability, arising either from hindered migration of the metal or from some kind of compound formation through the orifices of molecular dimensions[9] by which the voids are interconnected.

By virtue of their high chemical stability (particularly in organic media), and of their thermal stability, zeolites can be used at high temperatures, and are easily regenerated. In this respect they are superior to organic cationic ion-exchange resins, whose thermal stability is still limited[10] to 160–190°, whereas zeolites are stable up to 800° and above.

In recent years, zeolites in which some of the $AlO_4$ and $SiO_4$ tetrahedra are replaced by structural units containing Ge, Ga, Be, Mg, Cr, and other elements have been synthesised by isomorphous substitution. A comparison of the catalytic properties of these zeolites with those of the corresponding cationic forms of alumina–silica zeolites will provide valuable evidence on the relative contributions of the cationic and the anionic parts (sites) of the zeolites to their catalytic activity, and will reveal new ways of varying and controlling the properties of zeolite catalysts.

Research carried out during the past few years has led to the development of new, highly active catalysts, some of which have already found industrial application, whilst others are undergoing trials. The following new industrial catalysts — Durabead 5, a cracking catalyst almost 100 times as active as amorphous alumina–silica catalysts, the cracking catalyst[11] XZ-15, and also the isomerisation catalyst MB-5390 (SK-100) for n-alkanes, showing enhanced stability towards water and sulphur, and enabling reactions to proceed at temperatures 60–80 deg lower than existing bifunctional catalysts of the metal–acidic oxide type[12] — have been developed in the USA. In addition to their high activity and selectivity, these catalysts are remarkably stable towards impurities in the crude materials, particularly sulphur and nitrogen compounds, and heavy metals, which usually poison catalysts of other types.

These special features of zeolite catalysts are their most promising characteristics, and are the reason for the increasing scientific and practical interest in these materials.

## II. GENERAL INFORMATION ON ZEOLITES, AND ON SOME OF THEIR PHYSICOCHEMICAL PROPERTIES

Most of the synthetic zeolites, like all natural zeolites, are aluminosilicates†. These compounds can have a fibrous structure, a layer structure, or a three-dimensional (skeletal) structure. Zeolites with a layer structure are thermally unstable, and possess only moderate adsorption properties. The most valuable crystalline alumina–silica zeolites from the point of view of adsorption and catalysis are those with a stable three-dimensional skeleton, and the following discussion will be mainly confined to zeolites of this type.

Approximately forty natural zeolites have been described so far, but the total number of synthetic zeolites exceeds fifty[18]. The most interesting of these are the zeolites of types A, X, Y, L, S, P, E, mordenite, and others. Their general empirical formula can be written

$$M_{2/n}O \cdot Al_2O_3 \cdot x\,SiO_2 \cdot y\,H_2O,$$

where $n$ is the valency of the metal cation M, while $x$ is the $SiO_2/Al_2O_3$ molar ratio, and $y$ is the number of moles of water. The value of $x$ determines the structure and the properties of the zeolites. Thus, in a type A zeolite $x$ is close to 2.0, in a type X zeolite it varies from 2.2 to 3.0, in a type Y zeolite from 3.1 to 5.0 [18] (or to 6.0 according to other workers[8]), and in a synthetic mordenite values as high as 10 have been reported[19–21]. The zeolite lattice consists of $SiO_4$ and $AlO_4$ tetrahedra. As we have already pointed out, the aluminium–oxygen and silicon–oxygen tetrahedra in zeolites can be replaced by tetrahedra of other ions, e.g. $P^{5+}$, $Ga^{3+}$, $Ge^{4+}$, etc. These tetrahedra arrange themselves so as to form polyhedra. Thus, 8 tetrahedra can form a cube, 12 can form a hexagonal prism, and 24 can form a cubic octahedron. The unit cells of the zeolites are formed by the packing of these polyhedra. Voids appear between and within the polyhedra: these are interconnected by oxygen rings (orifices). The cross-sectional areas of these voids (pores) and orifices are of molecular dimensions, and are strictly constant for each type of zeolite. This property of zeolites accounts for their exceptionally high selectivity in adsorption and catalytic processes: whether or not the voids within the crystal are accessible to adsorbed molecules

† Zeolites in which aluminium has been replaced by gallium [13,14] or chromium [15,16], and the silicon by germanium [13], beryllium, or magnesium [17], have been synthesised and investigated. Their importance from the point of view of catalysis will be discussed below.

depends on the size of the latter (critical diameter). The sizes of the large voids and of their interconnecting orifices are set out in Table 1 for various zeolite samples. More detailed discussions of zeolite structure[3,4,22-30] and of the critical diameters of molecules[22] have been published.

The adsorption properties of zeolites become apparent only after dehydration, because the voids in the crystals are filled with water molecules during preparation. Zeolitic water can be removed from the crystals by heating to 300–350°, which does not affect the crystal lattice structure of most zeolites. The ease of dehydration depends on the ion-exchange form of the zeolite. Thus, the calcium form is considerably more resistant to dehydration than is the sodium form[29]. However, zeolites retain small amounts of water even after treatment at 500°. Table 2 lists the water losses reported[31] for some zeolites on heating from 500° to 1000°.

After dehydration, zeolites have a high adsorption capacity. The combined volume of the voids can amount to 50% of the total volume of the crystals[23]. An important property of the zeolite lattice is its high thermal stability. Thus, NaA zeolite is stable up to 700°, and NaX up to 750–800°. The thermal stability of zeolites increases with increasing silicon content[32], and for samples of a given type it is strongly dependent on the nature of the cation, increasing with the radius of the latter[33,34]. As noted above, the cations which compensate the negative charges of the $AlO_4^-$ tetrahedra can undergo ion exchange. The character of the exchange process is determined by the nature, size, and charge of the cations, and by the structure type of the zeolite[35-41]. Cation exchange takes place most effectively in an alkaline medium[42]. Large cations show an ion-sieve effect, which affects the extent and the rate of exchange[35,36,43]. The long-range order of the zeolite crystal lattice is sometimes disrupted by cation exchange. This effect is very sensitive to the pH of the solution in which the exchange is taking place: many zeolites, such as types A and X, lose their structure in acid media (below pH 5). The stability of the structure is also a function of the extent of ion exchange.

The presence of mobile cations in zeolites gives rise to electrical conductivity[23,44,45], the activation energies for conduction and the resistivities being less than in other types of crystal.

TABLE 1. Diameters of large voids and of their interconnecting orifices in some zeolites.

| Zeolite | LiA | NaA | KA | CaA | NaX (NaY) | CaX (CaY) | CaM * | H–M |
|---|---|---|---|---|---|---|---|---|
| Diameter of large void, Å | 12 | 11–12 | 11 | 11 | 11–13 | 11–13 | 7 ** | 7 |
| Size of orifices, Å | 4.4 | 4.0 | 3.3 | 5.0 | ~9 | ~8 | 4 | 6.6 |

* CaM and H–M are the calcium and the hydrogen forms of synthetic mordenite.

** Length of large channel.

TABLE 2. Thermogravimetry of some zeolites.

| Zeolite | NaX | MgX | NaY | MgY | CaY | SrY | BaY |
|---|---|---|---|---|---|---|---|
| Degree of exchange, % | — | 70 | — | 72 | 72 | 77 | 77 |
| Water lost on heating from 500° to 1000°, wt. % | 0.27 | 1.04 | 0.14 | 0.88 | 0.88 | 0.45 | 0.25 |

As well as the various cationic forms, the hydrogen and the decationated forms of molecular sieves are of great importance in catalysis. These modifications have a high catalytic activity[19-21,46], are more stable towards acids than the cationic forms[47], and show some other specific properties. Replacement of a cation by a proton by ion exchange in an acid medium is possible only with high-silica zeolites, such as mordenite[27]: most other zeolites decompose under these conditions. Barrer suggested the use of the ammonium form[48], which undergoes a reaction giving rise to the H-zeolite when heated in oxygen:

$$4\,(-O^- \ldots NH_4^+) + 3O_2 \rightarrow 4\,(-O^- \ldots H^+) + 6\,H_2O + 2N_2.$$

The hydrogen zeolite can be prepared from the ammonium form also by decomposition under vacuum baking conditions[49]:

$$NH_4X = H{-}X + NH_3 \text{ (X is the anionic skeleton of the zeolite).}$$

Treatment of silver zeolites with aqueous solutions containing $H^+$ ions to replace the $Ag^+$ ions and anions to precipitate the silver going into solution also produces the hydrogen forms[48,50]. An aqueous solution of pyridine hydrochloride[50] can be used. In practice, H-forms are most frequently prepared from the ammonium zeolites. The hydrogen (or protonated[23]) modification has the characteristic lattice of the starting zeolite, but it has more open channels than the cationic modifications. The hydrogen form is unstable at high temperatures, and is converted into the decationated form[46] by further dehydration. Under these conditions the crystal lattice of some zeolites is disintegrated, depending on the extent of exchange. Thus, the structure of zeolite X does not break down if the exchange of $Na^+$ by $NH_4^+$ is limited[51] to 30%. With a type A zeolite, decationation is possible only up to 10%, whereas with a type Y zeolite up to 90% can be achieved[51]. Zeolites can be decationated also by electrodialysis[17]. It must be stressed that the nature of the decationated form of crystalline aluminosilicates has not been definitely established. We can only report[46] that three-coordinated aluminium atoms (Lewis-acid regions) and unpaired electron spins are present in decationated samples of zeolite Y.

## III. PREPARATION OF ZEOLITE CATALYSTS

Zeolite catalysts are prepared mainly by three methods — (1) ion exchange, (2) impregnation, and (3) introduction of the catalytic component during synthesis (crystallisation) of the zeolite.

The exchange of sodium cations in prepared samples of zeolites by cations of other elements (or by $H^+$) and the decationation of these samples have been discussed above. These treatments yield various cationic forms (or the decationated form), possessing, as has already been said, different catalytic properties. These modifications can be treated as one of the types of zeolite catalyst.

Cation exchange can be used also to introduce metals into the zeolite structure. However, the method is restricted to elements whose cations can be reduced to the metal (by hydrogen or by alkali metals). For example, nickel-exchanged zeolite (or a zeolite containing complex cations) can be reduced by hydrogen to atomic nickel[9] at high temperature (~ 500°). In addition to nickel atoms, protons are also formed, which compensate the negative charges of the alumina–silica skeleton in place of the nickel ions:

$$[AlO_4]_2^- Ni^{2+} + H_2 \rightarrow 2Ni^0 + 2\,[AlO_4]^- H^+.$$

The form in which the protons exist has not been accurately established: they may enter the structure as hydroxyls. Partial decationation of the zeolite by removal of water from the hydrogen form, produced as an intermediate, is also not excluded. The result is a zeolite containing deposited metal, or, as it is called, a metal-loaded zeolite [9,52-55]. Many types of these catalysts, containing metallic phases of most of the transition elements, can be prepared. Zeolites can be loaded with metals also by adsorption of appropriate volatile or soluble compounds, organic or inorganic, of the metals on the dehydrated zeolites, followed by thermal decomposition of the compounds. The latter should decompose with deposition of the metals at temperatures below the stability threshold of the crystal lattice. The following compounds can be used — carbonyls or hydrogen carbonyls (Fe, Co, Ni, Cr, Mo, W, Mn, Re), acetylacetonates (Cr, Cu, Ag, Au), halides (Ti, Hf, Zr), alkyl derivatives, and other organometallic compounds — and the preparation and use of a number of loaded molecular sieves have been described in the patent literature [56-63]. Oxidation of the metal (e.g. Zn or Cd) in a loaded zeolite in air or oxygen produces a zeolite loaded with the metal oxide.

In some cases, introduction (or deposition) of the catalytic agent after the zeolite crystals have been prepared is unsuitable. Thus, platinum cannot be introduced by ion exchange into a CaA zeolite having 5-Å orifices, because the available platinum compounds have low pH-values and are liable to disrupt the zeolite structure, while the cations of neutral platinum ammines are larger than 5 Å. In this case the catalytically active agent is conveniently introduced at the stage of preparation (crystallisation) of the zeolite [64].

The catalytic agent can also be deposited on the zeolite particles as an external coating [65]. In multicomponent contact materials the catalytic functions of the zeolite may either combine with those of the added component or disappear. Therefore, in spite of the fact that the properties of zeolites can vary according to the conditions of application and treatment, it is probably useful to differentiate between catalysts in which the zeolites act as inert carriers for the active components and polyfunctional catalysts in which the zeolite substrate performs a specific function.

Problems of catalyst activation are closely bound up with catalyst preparation. Obviously, no single method of processing can be generally applicable to all catalysts. We can only stress the fact that removal of the water from the catalysts (albeit partial) is essential in every case, since only then are the zeolites able to adsorb molecules in their intracrystalline voids, which are the main site of reactions on zeolite catalysts. The conditions, rate, and extent of dehydration depend on the particular catalyst and on the particular process.

## IV. APPLICATIONS OF ZEOLITE CATALYSTS

The first reports of the use of synthetic zeolites as catalysts were published [46,66,67] in 1960. In the following years the properties of contact materials based on various cationic forms of zeolites (types A, X, Y, mordenite, etc.) were investigated in a number of reactions, the catalysts being used both individually and in admixture, and also with additions of catalytically active metals and their compounds. These reactions, and the specific features of the zeolite catalysts, will be discussed in the following subsections.

### 1. Catalytic Properties of Purely Synthetic Zeolites

Weisz and Frilette [67] discovered that NaX and CaX zeolites are more active towards the cracking of n-decane at 470° than are the standard alumina–silica catalysts containing 10% of $Al_2O_3$. The calcium form of the zeolite was more active than the sodium form, and gave products similar to those obtained in the presence of the alumina–silica catalyst. In contrast, the products obtained on NaX contained no iso-compounds, but double the quantity of alkenes instead. Furthermore, NaX was inactive towards the dealkylation of cumene even at 510°, whereas CaX was a powerful catalyst for this reaction even at 465°. The latter material also brought about the conversion of α-pinene into camphene, but this did not occur on NaX. To account for these results, the authors suggested [68] that the reactions proceed by different mechanisms on these catalysts — by a radical mechanism on NaX, and by a carbonium ion mechanism in the presence of CaX.

The influence of the degree of exchange of $Na^+$ by $Ca^{2+}$ in a type X zeolite on the catalytic activity towards the cracking of n-decane has been investigated [69]. It was shown that the activity increases with decrease in the $Na_2O$ content of the zeolite, but it was pointed out that the deactivating effect of sodium is less marked in zeolite catalysts than in the alumina–silica catalyst.

The CaX zeolite is much less active [70] towards the cracking of cumene than is an alumina–silica catalyst of the Houdry type, but the course of the reaction is the same. Cumene was found to be adsorbed approximately twice as strongly as benzene on the CaX zeolite, whereas on alumina–silica catalysts the adsorption coefficients are nearly the same [70].

The cracking of cumene has been used as a model reaction in many studies of the catalytic activity of synthetic zeolites [31,51,71-76].

Tsitsishvili and his coworkers [71] investigated the activity of NaX, CaX, and HX zeolites, and concluded that the reaction on these catalysts was sterically hindered.

Topchieva and her coworkers [72-74] studied the catalytic activity of synthetic X and Y zeolites, and found that NaX had negligible activity: replacement of $Na^+$ ions by $Ca^{2+}$ increases the activity in proportion to the extent of exchange. There was also an appreciable increase in activity on increasing the $SiO_2/Al_2O_3$ ratio in the zeolite. The highest rate constant was obtained with decationated samples of the Y zeolite. The authors did not observe significant adsorption of propene on the zeolites, which suggests that propene cannot inhibit the cracking of cumene on these catalysts, whereas it is known to inhibit the reaction on amorphous alumina–silica catalysts. Hence, they concluded [72,74] that the kinetic mechanism of cumene cracking is probably different on the two types of catalyst.

The adsorption of quinoline on zeolites was examined [73] in order to throw light on the nature of the active centres. With decationated samples of zeolite Y the activity initially decreased in proportion to the amount of quinoline adsorbed, and remained constant thereafter. This trend in the activity of decationated zeolites led the authors to postulate the existence of at least two types of active centre on the surface — aprotic centres, associated with aluminium atoms in the tervalent state, and $AlO_4$ tetrahedra.

Schwab and Sieb [75] showed that the activation energy for cumene cracking of the cationic forms of zeolite X examined

($Mg^{2+}$, $Ca^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Mn^{2+}$) passes through a minimum as $Na^+$ is gradually replaced by the bivalent cation (with the exception of $Cd^{2+}$, with which the activation energy increases continuously). The authors' explanation is that at high degrees of exchange the replacement occurs in deep layers of the zeolite, which are not accessible to the cumene. These results are somewhat unexpected: after a certain amount of exchange, one would have expected the activation energy to remain constant.

Among the univalent cationic modifications of zeolite X (the Li, Na, K, and Rb forms), the lithium form is the most active towards cumene cracking[76] at 500°, and is comparable to an industrial alumina–silica catalyst. The authors[76] point out the proportionality between catalytic activity and the force field of the cation, and suggest that the cations act as active centres in the zeolites.

Rabo and his coworkers[31] report that the activity of Y zeolites ($SiO_2/Al_2O_3$ = 5) in the cracking of cumene increases in the sequence NaY < BaY < SrY < CaY ≃ MgY ≃ ≃ BeY, i.e. in the opposite order to the radii of the corresponding cations. Thus, a direct link exists between catalytic activity and the polarising power of the cations, which increases with decrease in their radius.

The activity of the centres in decationated type Y zeolites varies[51], being highest in the samples containing the greatest number of decationated regions. The authors account for the non-equivalence of the centres by three factors — (1) the presence in the zeolites of three types of crystallographically different sites for the $Na^+$ ions, and probably also for the decationated sites, (2) interaction between the centres, determined by the proximity of the sites, and (3) the presence of three-coordinated unsaturated aluminium centres, in addition to $AlO_4^-$ tetrahedra, in decationated zeolites. The same workers have shown[77] that irradiation of decationated zeolites lowers the activation energy for the cracking of cumene.

The hydrogen form of synthetic mordenite has a high catalytic activity for hydrocarbon cracking[78–81]. The fission capabilities of this catalyst in the cracking of n-decane[78] are similar to those of CaX zeolite[67]. Synthetic mordenite in the H-form cracks gas oil, n-heptane, 2,4-dimethylpentane, and methylcyclohexane faster than does the commercial alumina–silica catalyst[81], giving a higher proportion of light and branched hydrocarbons among the products. Natural mordenite, previously treated with acid and converted into the hydrogen form, becomes active in cracking, alkylation, and isomerisation reactions at relatively low temperatures[82,83]. For example, the cracking of n-hexane occurs at a temperature as low as 200° with formation of saturated compounds, and benzene is converted into toluene and ethylbenzene[83] at 400°. Butane and cyclohexane rapidly isomerise to isobutane and methylcyclopentane respectively at ~ 200°, and the authors stress the fact that under these conditions deactivation of the catalyst is very slow. Thus, at 260° and under atmospheric pressure, cyclohexane (in a stream of helium) is 11.5% converted into the isomer and 0.9% into side-products. None of these reactions occurs on amorphous alumina–silica catalysts under the stated conditions. The authors conclude that acid mordenite is more closely similar to $AlCl_3$ promoted with HCl than to an amorphous alumina–silica catalyst[83].

Some interesting features of the cracking of alkanes on synthetic zeolites have been observed[84–88]. In the presence of CaA zeolite, n-dodecane decomposed without formation of cyclic compounds, which did, however, form on NaX and CaX. The reaction products obtained in the presence of CaA also contained very small amounts of branched hydrocarbons[84]. Both dehydrocyclisation and isomerisation reactions take place in the voids of the CaA molecular sieve, but because of the small size of the orifices the resulting hydrocarbons cannot escape from the voids and undergo further transformations[85,86].

Many workers have demonstrated the high activity towards hydrocarbon cracking of the rare-earth cationic forms of zeolites X and Y and of mixed metal–acid crystalline aluminosilicates[89–96]. These catalysts, in which some of the $Na^+$ ions have been replaced by $H^+$ and some by multivalent cations ($Ca^{2+}$, $Mn^{2+}$, rare-earth elements, etc.), show enhanced activity, high selectivity, and good stability[89]; they are used in the preparation of the new industrial cracking catalyst[11,89] Durabead 5.

As was mentioned above, zeolites can also catalyse many reactions besides cracking. Their polymerisation properties were the first to be observed, because these became apparent (as "parasitic" catalytic activity) when the zeolites were used for drying alkenes. Molecular sieves can be arranged in the following sequence of catalytic activity for the polymerisation of propene[97–99]: CaX > > NaX > CaA > NaA > KA = 0. The reactivity of alkenes increases iin the sequence $CH_2{:}CH_2 < CH_3.CH{:}CH_2 <$ $< (CH_3)_2C{:}CH_2$, which is consistent with the reactivities of alkenes towards an acidic catalyst in ionic polymerisation. The composition of the polymerisation products (e.g. of propene) is also similar to the composition of the products obtained when phosphoric acid on kieselguhr is used as the catalyst. Norton[97–99] suggests that the action of zeolites in the polymerisation process is bound up with the presence of acidic regions in these materials.

The polymerisation of gaseous and liquid (low-boiling) $C_2$–$C_6$ monoalkenes on crystalline alumina–silica catalysts has been proposed[100] as a method for the production of high-octane fuels for reciprocating internal-combustion engines. In the presence of CaA zeolite, isobutene polymerises even at room temperature and atmospheric pressure to give a product containing 90 vol.% of the trimer and 10 vol.% of the dimer[101].

Crystalline aluminosilicates can also catalyse isomerisation of the double bond in alkenes[102–104]. Thus, but-1-ene on CaA zeolite, at atmospheric pressure and a temperature of 80°, undergoes 71% conversion into but-2-ene, and at 220° the yield of but-2-ene reaches 85%; 2-methylbut-1-ene is 88% converted into 2-methylbut-2-ene at 100°.[103] The activity of zeolites towards the isomerisation of alkenes is increased by $\gamma$-irradiation[77,102]. The high (up to 73%) and stable (unaffected by operation for 24 h) catalytic activity of CaA zeolite in the isomerisation of 2-methylpent-1-ene is particularly interesting[104].

Alkanes and cyclic hydrocarbons also can be isomerised on synthetic zeolites. Thus, NaX catalyses[105] the conversion of cyclopropane into propene. Cyclohexane is converted into methylcyclopentane on CaX zeolite, the yield being increased by recycling[106]. Zeolites of types X and Y in their bivalent cationic forms promote the isomerisation of n-alkanes[31].

Synthetic zeolites catalyse also the conversion of alcohols. Depending on the nature of the catalyst and on the experimental conditions, alcohols are converted into ethers[107–110] or alkenes[76,78,83,90,97,107,109,111–115], or alternatively they undergo mainly dehydrogenation with formation of carbonyl compounds[16,57]. Ethers are obtained when

the zeolite used has fairly large pores, at low temperatures, and with relatively high flow rates. Dehydrogenation of alcohols was observed on type A zeolites containing chromium introduced by isomorphous substitution[16]. In every other case the alcohols suffered dehydration with the formation of alkenes. The process is sometimes complicated by side reactions, such as polymerisation and isomerisation of the double bond and of the skeleton of the resulting alkenes, hydrogenation with formation of alkanes, etc. For the dehydration of propan-2-ol[71], the zeolites can be arranged in the series HX > NaX > CaA. The reaction took place[71] at temperatures below 250° on the NaX sample, even though Frilette and Munns[114] were unable to observe any reaction even at 300°. This discrepancy may have been caused by the use[71] of a contaminated or partly hydrolysed zeolite. However, it has been reported that the NaX zeolite dehydrates alcohol in the presence of carbon dioxide. The active centres are said[114] to result from the chemisorption of $CO_2$ on the zeolite. A similar promoting effect of carbon dioxide on zeolite catalysts has been observed also in the cracking of alkanes, alkenes, aromatic and naphthenic hydrocarbons, and their mixtures, in the isomerisation and polymerisation of alkenes, in the polymerisation of terpenes, and in a number of other reactions[110].

The dehydration of various alcohols on NaX and CaX zeolites has been investigated[111,112]. On NaX the chain length and the amount of chain branching do not affect the degree of conversion of the alcohols: pentanol, 3-methylbutan-1-ol, and nonanol are dehydrated to the extent of 53–56% at 275° and a space velocity of 4 $h^{-1}$. On CaX the conversion of pentan-1-ol was significantly higher than on NaX, but the products contained a large proportion of saturated hydrocarbons (mainly isopentane), increasing rapidly with temperature, whilst the yield of pentenes decreased. Furthermore, isomerisation of the skeleton and cracking were much more extensive on this catalyst than on NaX.

The CaY zeolite ($SiO_2/Al_2O_3$ = 3.4) has a high activity towards the dehydration of $C_2$–$C_4$ aliphatic alcohols and cyclohexanol[109]. All the normal primary alcohols were completely converted into the corresponding alkenes on this catalyst at 250°. Cyclohexanol was dehydrated smoothly and selectively: 68% of cyclohexene was obtained even at 150°, and at 170° the reaction was quantitative. With n-butanol and isobutanol, the resulting alkenes underwent extensive polymerisation under the experimental conditions[109].

The zeolites CaX and CaY showed remarkable behaviour in the dehydration of t-butyl alcohol[115]. The fully anhydrous zeolites had very low activity, which increased, however, as the water content of the catalyst was increased. The highest activity was observed with samples containing one water molecule per cation in the unit cell. Promotion by water was reported also in the cracking of n-hexane on the rare-earth cationic form of type Y zeolite[116]. These observations should help to elucidate the mechanism by which zeolite catalysts operate.

According to the patent literature[117], molecular sieves show high selectivity and thermal stability as catalysts for the hydration of ethylene oxide to ethylene glycol.

Several papers have been published on the use of synthetic zeolites as alkylation catalysts. A patent suggests various cationic forms of the X zeolite for the alkylation of aromatic hydrocarbons by alkenes[118]. There is evidence[8] that, unlike the conventional acidic alkylation catalysts, which rapidly lose their activity in the presence of sulphur and oxygen compounds, zeolites show a high activity in the presence of these impurities even without added metallic cocatalysts. It is pointed out that thiophens and phenols can be alkylated rapidly and with good selectivity on these catalysts[7,8]. Minachev and his coworkers[119–127] studied the reactions of aromatic hydrocarbons with alkenes and alcohols in the presence of X and Y zeolites of different compositions produced in the Soviet Union and also in the presence of synthetic mordenite. They found[120,121] that the activity of zeolites of similar structure (X and Y) in the alkylation of benzene by propene at atmospheric pressure increases with increase in the $SiO_2$ content. They also suggested[120] that, as in the case of amorphous alumina–silica catalysts, an optimum $Al_2O_3$ content should exist in zeolites. A comparative study of the behaviour of the calcium forms of Y zeolite obtained from NaY by exchange with calcium chloride, nitrate, and acetate led the authors to conclude[121] that the nature of the anion of the salt has practically no effect on the activity of the catalyst. It is the cation which plays the key role in determining the catalytic activity of zeolites[121,125,127].

It is evident from Table 3 that NaY zeolite has negligible activity towards alkylation under the stated conditions: only by raising the temperature to 400° and by decreasing the flow rate of the reaction mixture to one-third of its value could the yield of cumene be raised[121] to 10%. Bivalent and tervalent cationic forms are very active, the activity of these zeolites varying monotonically with the polarising effect of the cation: the greater the charge on the cation and the smaller its radius, the higher is the polarising effect of the cation and the more active is the catalyst. The bivalent modifications with comparable degrees of cation exchange can be arranged in the series BaY < SrY < CaY ≃ CdY ≃ MgY. The tervalent cationic forms are more active (on the basis of a single cation in the unit cell) than samples with bivalent cations, but they are less stable[125]. The activities of the pure crystalline aluminosilicates of the rare-earth elements with similar degrees of exchange are practically identical (Table 3).

TABLE 3. Alkylation of benzene by propene* at 250° on various cationic forms of Y zeolite[121,127] having $SiO_2/Al_2O_3$ = = 4.2, with feed rate of mixture 10.2 moles litre$^{-1}$ $h^{-1}$ (0.6 $h^{-1}$ with respect to $C_6H_6$) and $C_6H_6/C_3H_6$ = 2.5 : 1 (molar).

| Zeolite | Degree of exchange of $Na^+$ by $M^{n+}$, equiv. % | Radius of cation, Å | Yield of monopropylbenzenes, % (based on propene) | Zeolite | Degree of exchange of $Na^+$ by $M^{n+}$, equiv. % | Radius of cation, Å | Yield of monopropylbenzenes, % (based on propene) |
|---|---|---|---|---|---|---|---|
| NaY | — | 0.98 | trace | LaY | 60 | 1.22 | 35.2 |
| DY ** | 75 | — | 54.2 | $Ce^{3+}$Y | 61 | 1.18 | 53.1 |
| MgY | 80 | 0.78 | 37.6 | $Pr^{3+}$Y | 60 | 1.16 | 51.0 |
| CaY | 75 | 1.06 | 32.8 | $Nd^{3+}$Y | 63 | 1.15 | 51.0 |
| SrY | 80 | 1.27 | 10.6 | SmY | 60 | 1.13 | 52.5 |
| CdY | 76 | 1.03 | 35.4 | mixed REE–Y**** | 15 wt. % of oxides | — | 45.3 |
| BaY | 62 | 1.43 | 1.4 | alumina–silica | — | — | 13.7 |
| AlY *** | 57 | 0.57 | 45.5 | | | | |

* Propane–propene fraction containing 75 vol. % of propene.
** Decationated form.
*** At 300°.
**** REE = rare-earth element.

Thus there is no need to use pure compounds for the preparation of rare-earth catalysts: a contact material having approximately the same activity and selectivity can be prepared from a mixture of salts of composition similar to that of the technical mixtures of rare-earth metal chlorides [127], which makes these catalysts much more readily available. The highest yield of monopropylbenzenes (containing 93–98% of cumene) is obtained with the decationated zeolite DY. An industrial amorphous alumina–silica cracking catalyst is less effective by factors of 1.5–3.5 than zeolites with sufficiently wide orifices leading to crystal voids [120,121].

The extent of exchange of sodium ions by multivalent cations also has a marked influence on the activity and selectivity of zeolite catalysts towards alkylation [121,125,127]. The yields of monopropylbenzenes and all other alkylbenzenes increase as the proportion of $Na^+$ ions exchanged is increased, but not uniformly: this suggests that the cation sites in the zeolite are not equivalent. Thus, in the case of calcium [121,125], samples with degrees of exchange up to 40–45% have a low activity (Fig. 1); at around 50% exchange we observe a sharp discontinuity in the increase in activity, and the conversion of propene approaches 100%: with further replacement of $Na^+$ by $Ca^{2+}$ the yields of cumene and alkylbenzenes increase much more slowly, and the yield of polyisopropylbenzenes drops as a result of the change in the selectivity of the catalyst. A similar state of affairs has been reported [127] for $Nd^{3+}$ cations, the only difference being that the neodymium zeolites exhibited considerable activity at 20–30% lower degrees of exchange of the $Na^+$ ions than in the corresponding calcium zeolites. This is probably due to the higher affinity of the $Nd^{3+}$ cations (as compared with the $Ca^{2+}$ ions) for the catalytically active regions of the zeolite, and to the greater polarising effect of the tervalent cations [127]. The use of zeolites with a high degree of exchange allows the reactions to proceed under milder conditions, and leads to improved catalyst stability. Thus, the temperature had to be raised by 150 deg to obtain the same yield from an NdY zeolite of 21% degree of exchange as from a catalyst containing three times that amount of rare-earth elements [127].

The alkylation of benzene by ethylene and by some alcohols [121,124], and of homologues of benzene by ethylene and by propene [121,124,126], has been investigated. The results

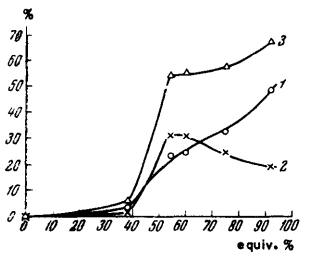



Fig. 1. Influence of the degree of exchange of $Na^+$ by $Ca^{2+}$ (abscissa), at 250° with a feed rate of the mixture of 10.2 moles litre$^{-1}$ h$^{-1}$ (0.6 h$^{-1}$ with respect to $C_6H_6$) and a molar ratio of $C_6H_6 : C_3H_6$ = = 2.5, on the yield of products of the alkylation of benzene by propene (ordinate):
1) cumene; 2) polyisopropylbenzenes; 3) alkylbenzenes (monoisopropylbenzenes + polyisopropylbenzenes).

TABLE 4. Alkylation of aromatic hydrocarbons by alkenes and alcohols on CaY zeolite, having $SiO_2/Al_2O_3$ = 4.2 and degree of exchange > 90% at atmospheric pressure.

| Aromatic hydrocarbon | Alkylating agent | Experimental conditions: temp. | Experimental conditions: feed rate of reactant mixture, moles × litre$^{-1}$ h$^{-1}$ | Experimental conditions: A : B molar ratio | Products | Yield, % |
|---|---|---|---|---|---|---|
| Benzene | ethylene | 400° | 5.1 | 2 | ethylbenzene<br>diethylbenzenes | 41.1<br>6.8 |
| Benzene | propan-1-ol | 250° | 3.5 | 6 | isopropylbenzene<br>n-propylbenzene<br>polyisopropylbenzenes | 70.4<br>4.4<br>1.2 |
| Benzene | ethanol | 325° | 3.6 | 6 | ethylbenzene<br>diethylbenzenes | 71.5<br>4.7 |
| Benzene | propan-2-ol | 250° | 3.5 | 6 | isopropylbenzene<br>n-propylbenzene<br>polyisopropylbenzenes | 72.8<br>2.8<br>2.9 |
| Toluene | ethylene | 375° | 5.1 | 2 | ethyltoluenes<br>xylenes, ethylbenzene, polyalkylbenzenes | 40.8<br>20.6 |
| Toluene | propene | 250° | 8.7 | 5.3 | monoisopropyltoluenes<br>polyalkylbenzenes | 74<br>3.7 |
| Ethylbenzene | propene | 250° | 7.5 | 5.3 | ethylmonoisopropylbenzenes<br>polyalkylbenzenes | 83.0<br>1.8 |
| Isopropylbenzene | propene | 250° | 9.9 | 5.3 | di-isopropylbenzenes<br>polyisopropylbenzenes | 85.1<br>3.2 |

of experiments made under the optimum conditions are given in Table 4. The yields of products are calculated on the basis of the alkenes (or alcohols) used in the reaction. In the absence of alkenes, homologues of benzene undergo disproportionation of their alkyl groups on CaY zeolite [121].

Hydrogen sulphide is oxidised to sulphur on NaX zeolite [66]. It has been found [128] to react with oxygen in the voids of zeolites, to give products which vary according to the experimental conditions and to the nature of the catalyst. Hydrogen sulphide is oxidised to sulphur trioxide at 100° on an NaA molecular sieve and at 200° on a CaX zeolite. Zeolites catalyse the vapour-phase reaction between methyl propionate and formaldehyde with formation of methyl methacrylate [129], and the condensation of organosilicon compounds [130]. Finally, it has been shown [51] that the decationated form of zeolite Y can catalyse the hydrogen–deuterium reaction. The activity of the catalysts can be increased by previous irradiation [77].

## 2. Zeolites as Carriers of Active Components

Under certain conditions, the zeolite substrate does not show any catalytic properties, but its adsorption properties can nevertheless have a profound effect on the activity, selectivity, and stability of catalysts. Hydrogenation is one of the most important applications of catalysts of this type. Thus, the hydrogenation of acetone to propan-2-ol has been achieved [60] on a nickel-loaded zeolite, and the selective hydrogenation of acetylene to ethylene [131] on a copper–zeolite catalyst.

Many workers [132] have examined the properties of nickel–zeolite catalysts in hydrogenations involving unsaturated hydrocarbons. A 3.8% Ni–NaA sample, prepared by cation exchange, showed high selectivity: n-octene was hydrogenated to the extent of 81.5%, whilst isoalkenes and benzene suffered practically no hydrogenation at all. The explanation is that the latter cannot penetrate to the inner voids of the zeolite, and contact the nickel. On the other

hand, a 5.8% Ni–NaA catalyst prepared by deposition effected 66.6% hydrogenation of benzene at 180°. The degree of conversion of alkylbenzenes was considerably lower (30–36%). Cyclohexene was not hydrogenated on the latter catalyst, but suffered irreversible catalytic changes (87%), whilst on a nickel-free zeolite it remained unchanged[132].

Several investigations of the hydrogenation of aromatic hydrocarbons on zeolites containing platinum-group metals have been published[7,8,63,123]. Minachev and his coworkers[123] showed that these catalysts can be arranged in the sequence

0.5% Rh/CaY > 0.5% Ir/CaY > 0.5% Pd/CaY.

as regards their activity towards the hydrogenation of benzene. Increasing the $SiO_2/Al_2O_3$ ratio in the zeolite has no effect on the activity of the catalysts. Equally unimportant is the nature of the cation ($Na^+$ or $Ca^{2+}$) in the zeolite. This statement applies only up to a definite temperature, because with rise in temperature hydrogenation may be accompanied by hydroisomerisation of benzene to methylcyclopentane[123]. Under milder experimental conditions, the nature of the cation may have a significant effect[8].

As Table 5 shows, diethylbenzene is hydrogenated almost quantitatively on both palladium–zeolite catalysts at 30 atm pressure. At and below 18 atm, the sample prepared from CaY zeolite is the more active. The high selectivity and the stable activity of these catalysts are stressed[8]. Zeolite catalysts show a greater selectivity than the conventional hydrogenation contact materials towards the hydrogenation of oils of high molecular weight[133].

The unusually high stability of zeolite catalysts towards sulphur-containing catalyst poisons is of great practical importance. Thus, acetylene was almost fully hydrogenated to ethane in the presence of hydrogen sulphide, and the catalysts (containing nickel or palladium) suffered no loss of activity for several hours[8].

Hydrodesulphurisation is another reaction in which loaded zeolite catalysts are used. A hydrorefining catalyst with enhanced activity is obtained[134] by introducing cobalt as a cation into the zeolite and then impregnating the product with molybdenum oxide ($MoO_3$). Zeolite catalysts[8] containing small amounts of a noble metal make possible the hydrodesulphurisation of crude products having appreciably higher final boiling points than with conventional hydrofining catalysts.

Metal–zeolite catalysts have been studied also in the hydrodealkylation of alkylbenzenes[135–137]. Thus, 51.8 mole% of benzene was obtained[135] at 550° from a mixture of toluene and hydrogen (molar ratio $H_2$ : CH = 20) in the presence of zeolite Y containing 0.5 wt.% of platinum. The ease with which methyl groups can be removed is stated[137] to decrease in the sequence cumene > ethylbenzene > toluene, whilst the extent of hydrogenolysis of the aromatic ring increases in the same order. Addition of 0.5% of sodium to an Ni–CaA catalyst lowered the extent of hydrogenation and hydrogenolysis of the aromatic ring, and left its activity towards hydrodealkylation unaffected in the case of toluene but lowered it in the case of cumene and ethylbenzene.

TABLE 5. Hydrogenation of aromatic hydrocarbons on metal–zeolite catalysts[8].

| Hydrocarbon | Diethylbenzene | | | | | | Benzene |
|---|---|---|---|---|---|---|---|
| Catalyst | 0.5% Pd/NaY | | | 0.5% Pd/CaY | | | 0.5% Rh/NaX |
| Temperature, °C | 215 | 215 | 215 | 215 | 215 | 215 | 210 |
| Space velocity, $h^{-1}$ | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 2.0 |
| Molar ratio $H_2$/CH | 16 | 16 | 16 | 16 | 16 | 16 | 5 |
| Pressure, atm | 30 | 18 | 7 | 30 | 18 | 3.5 | 0 (1 atma) |
| Conversion, % | 99 | 88 | 40 | 99 | 99 | 60 | 10 |

Several workers have examined the possibility of using zeolites as dehydrogenation catalysts for n-alkanes[59,84,85,87,88]. Zeolite X containing 1.95 wt.% of chromium is recommended[59] as a catalyst for the dehydrogenation of propane. Galich et al. studied the activity of catalysts, prepared from zeolites A and X, towards the dehydrogenation of n-hexane[85,87,77] and n-heptane[87], and found that the activity for these particular reactions was low[88]. The unmodified zeolites caused mainly cracking of the initial hydrocarbons, but catalysts containing $Cr_2O_3$ were selective for dehydrogenation. The selectivity of the contact materials was improved by adding iron and chromium oxides to the zeolites, and also by replacing sodium and calcium by nickel, cobalt, zinc, chromium, and copper cations, and by protons. The catalysts prepared from type A zeolites, which hinder the passage of aromatic hydrocarbons and isoalkanes into the product phase, were more selective than those prepared from type X zeolites. In every case the catalytic activity depended on the adsorption properties of the zeolites and of their modifications, irrespective of the method of preparation[88].

Zeolites can also be used as the basis of oxidation catalysts: thus, crystalline aluminosilicates loaded with copper, silver, or gold catalyse the oxidation of ethylene to ethylene oxide[56], and a zeolite containing $TiO_2$ catalyses the vapour-phase oxidation of anthracene to anthraquinone[58]. A zinc-loaded zeolite has been proposed as a catalyst for the synthesis of methanol[52], and zeolites containing metals of the iron subgroup (Fe, Co, Ni) have been proposed as contact materials for the synthesis of ammonia, the Fischer–Tropsch synthesis, and other processes[60]. Cadmium oxide on a zeolite promotes the dehydrogenation of alcohols[57].

### 3. Multifunctional Multicomponent Zeolite Catalysts

These are, perhaps, the catalysts of greatest practical importance, for they are used in the isomerisation of n-alkanes, hydrocracking, reforming, and various other processes, which account for the bulk of the high-tonnage production in the catalytic processing of petroleum hydrocarbons.

The high activity of zeolite catalysts in the isomerisation of n-pentane and n-hexane was recognised[46] in 1960. The zeolites examined included those of types X ($SiO_2/Al_2O_3$ = = 2.5) and type Y ($SiO_2/Al_2O_3$ = 5) in various cationic forms, containing 0.5 wt.% of platinum or palladium, and it was found that samples containing univalent cations are practically inactive. Catalysts based on the decationated and on the multivalent cationic forms of type Y zeolite were extremely active. They gave not only isomers containing a tertiary carbon atom, but also quite large amounts (11–15%) of 2,2-dimethylbutane. However, catalysts prepared from zeolites containing cations of valency 3 or higher were less selective than those with bivalent cations, and in some cases the activity fell off rapidly. Catalysts based on NaX and CaX zeolites showed practically no isomerisation activity, while decationated amorphous alumina–silica had a lower activity than DY and CaY. Studies of the effect of ion exchange showed that increasing the degree of exchange enhances the activity of the samples and allows the

reactions to proceed at lower temperatures[46]. The new isomerisation catalyst MB-5390 for the conversion of n-pentane, n-hexane, and their mixtures was developed from this work: it combines the advantages of the high-temperature (370–455°) catalysts, which give a high yield of isomers, with those of catalysts working at low temperatures (23–205°), which offer a longer useful life[12]. The activity of this catalyst did not fall off after 2000 h operation. Furthermore, the catalyst was insensitive to water and sulphur (at concentrations < 0.001%). It was subsequently shown[138] that a catalyst more resistant to sulphur is obtained if platinum is introduced into CaY zeolite by ion exchange rather than by the normal impregnation method.

Minachev and his coworkers[62,122,123,139-141] examined the properties of X and Y zeolites produced in the Soviet Union, of varying $SiO_2/Al_2O_3$ ratios, and containing metals of Group VIII of the Periodic Table (Pt, Pd, Ir, Rh, Ni). Some of their results are presented in Table 6. The sodium forms of the zeolites gave inactive catalysts, whereas the calcium and the decationated forms gave highly active catalysts. Contact materials based on zeolites having $SiO_2/Al_2O_3 = 4.2$ were more active than materials in which this ratio was 2.5 or 3.4.[123,141] By increasing the ratio of silica to alumina in the zeolite it was possible to raise considerably the yield of isomeric hexanes (including 2,2-dimethylbutane), and to lower the reaction temperature. The platinum and the palladium catalysts (0.5 wt.%) had similar activities, but on the rhodium and iridium catalysts hydrocracking of the initial hydrocarbons took place in addition to isomerisation of n-alkanes. Thus, on a 0.5% Rh/CaY catalyst ($SiO_2/Al_2O_3 = 3.4$) at 390° and 30 atm, with a space velocity of 1 $h^{-1}$ and a molar ratio of $H_2/n\text{-}C_6H_{14}$ = = 3.2, the quantities of isomeric hexanes and hydrocracking products were 25.8% and 21.9% respectively, whereas on the analogous iridium catalyst at 310° they became[123,139,141] 6.3% and 26.2%. Varying the concentration of palladium in the zeolite from 0.25 to 1 wt.% had little effect on the activity of the catalyst.

The isomerisation of cyclohexane followed the same pattern as the transformations of n-alkanes[141].

TABLE 6. Isomerisation and hydroisomerisation of hydrocarbons on zeolites containing Group VIII metals[141] (30 atm; space velocity 1 $h^{-1}$, molar ratio $H_2/CH = 3.2$).

| Catalyst | $SiO_2/Al_2O_3$ | t, °C | Yield of isomers, wt.% | Hydrocracking products, wt.% |
|---|---|---|---|---|
| | | n-Butane | | |
| 0.5% Pt/CaY | 4.1 | 400 | 27.0 | 3.2 |
| | | n-Pentane | | |
| 0.5% Pd/CaY | 4.1 | 360 | 50.9 | 3.8 |
| | | n-Hexane | | |
| 0.5% Pd/NaY | 4.5 | 350 | trace | — |
| 0.5 Pd/CaY | 3.4 | 400 | 58.0 | 3.2 |
| 0.5 Pd/CaY | 4.5 | 350 | 70.3 | 3.6 |
| 0.5 Pt/CaY | 3.4 | 400 | 59.4 | 3.8 |
| 0.5 Rh/CaY | 3.4 | 390 | 25.8 | 21.9 |
| 0.5 Ir/CaY | 3.4 | 310 | 6.3 | 26.2 |
| | | n-Heptane | | |
| 0.5 Pd/CaY | 3.4 | 360 | 47.2 | 10.3 |
| | | Cyclohexane | | |
| 0.5 Pd/CaY | 4.5 | 330 | 57.0 | 3.7 |
| 0.5 Ir/CaY | 3.4 | 330 | 4.0 | 52.0 |
| | | Benzene* | | |
| 0.5 Pd/CaY | 4.5 | 320 | 67.3 | 4.3 |
| 0.5 Ir/CaY | 3.4 | 320 | 5.8 | 60.0 |
| 0.5 Rh/CaY | 3.4 | 320 | 12.0 | 16.9 |

* Space velocity = 0.5 $h^{-1}$, $H_2/C_6H_6 = 5$.

The hydroisomerisation of benzene gave higher yields (up to 67.3%) of methylcyclopentane than could be obtained by the conversion of cyclohexane. In addition to benzene and the isomeric cycloalkanes cyclohexane was also present among the reaction products. The rhodium and particularly the iridium catalysts again showed a high activity towards hydrocracking: at 320° the former gave 16.9% and the latter ~60% of hydrocracking products, whilst hydroisomerisation occurred only to the extent of 12% and 5.8% respectively.

A comparison of zeolitic and conventional bifunctional isomerisation (hydroisomerisation) catalysts showed that the former are in many cases more active than the latter[141]. A given degree of conversion of hydrocarbons can be achieved on zeolite catalysts at temperatures 50–100 deg lower than on other bifunctional catalysts. Moreover, the former offer good selectivity and high stability[141]. Lastly, a metal–zeolite catalyst does not require promoters such as HCl or HF, which are normally introduced into the $Al_2O_3$ or added to the crude material. All these observations confirm that zeolite catalysts are superior to those currently used in industry for isomerisation reactions.

Some metal–zeolite catalysts, such as the rhodium and the iridium zeolites, show a high activity towards the hydrocracking of hydrocarbons under certain conditions[141]. These properties are found also in catalysts prepared from the rare-earth cationic forms of zeolites and the oxides or sulphides of metals in Groups VI and VIII of the Periodic Table[142,143]. Hydrocracking of high-boiling hydrocarbons can be realised also on zeolites containing metals of Group VIII.[144,145].

Zeolite reforming catalysts also have valuable properties[7,8,146,147]. Unlike platinum reforming catalysts, they are relatively insensitive to the presence of nitrogen bases in the crude material. Thus, they are unaffected for 150 h by up to 200 p.p.m. of nitrogen (in the form of quinoline) in the fraction undergoing reforming[8].

## V. SELECTIVITY OF ZEOLITE CATALYSTS

Data on the use of zeolite catalysts show that the main factors determining their activity are the nature and the degree of exchange of the cation in the zeolite, the structure of the zeolite lattice, the value of the $SiO_2/Al_2O_3$ ratio, and the sizes of the reactant and product molecules relative to the orifices in the zeolite. Allowance for these factors enables us to make a rational choice of zeolite catalysts having the properties required for specific reactions. Other conditions being the same, the relationship between the size of the molecules and the size of the orifices leading to voids in the zeolite is particularly important. Thus[64], n-hexane (critical diameter 4.9 Å) and 3-methylpentane (5.9 Å) are not cracked on zeolite NaA, in which the orifice size is 4 Å. On CaA zeolite (5 Å), only n-hexane is converted, while 3-methylpentane cannot gain access to the voids in the zeolite and does not react under the same conditions. When a mixture of n-hexane, 2-methylpentane, and 3-methylpentane is cracked on CaA zeolite, only the straight-chain hydrocarbon is converted. It is evident from these results that zeolites show high selectivity in respect of the size and shape of molecules, and that the active centres in zeolite catalysts are mostly located within the crystal voids. The term "intracrystalline catalysis"[64,67,68,78] originated from this effect. The intracrystalline nature of catalysis by zeolites is revealed

also by other examples. Thus, n-butanol is dehydrated to the same extent (~ 60%) at 260° on CaX zeolite (~ 8 Å) and on CaA zeolite[64]. But the degree of conversion of isobutanol (critical diameter > 5 Å) at the same temperature is 85% on CaX zeolite, and less than 2% on CaA. A similar state of affairs has been observed with s-butyl alcohol: this compound was 82% dehydrated on CaX at 130°, whereas no reaction occurred on CaA. However, on raising the temperature to 210° the compound was 45% dehydrated. This shows that, according to the conditions and to the reactivity of the molecules, the reaction can occur also on the outer surface of zeolites, although this surface accounts for only 3–5% of the total surface area. The same workers[64] have selectively hydrogenated propene (in an equimolecular mixture with isobutene) on a 0.31% Pt/CaA catalyst. At 343° and under atmospheric pressure the only product of the reaction was propane (yield ~ 70%), in spite of the fact that the two alkenes have identical reactivities towards hydrogenation. It should be noted that n-alkenes (propene, but-1-ene) could be hydrogenated even at 25°. Experiments with single alkenes showed that the active centres of the platinum are not accessible to the isoalkene, which explains why the latter was not hydrogenated.

A great deal of work has been done on the selectivity of zeolite catalysts[85,90,106,107,122,148-151]. The dehydration of ethanol on CaA zeolite gave mainly ethylene, whereas the chief product of the reaction on CaX under comparable conditions was ether[107]. Selective oxidation of n-alkanes mixed with isomers can be effected[148,150].

Individual molecules which penetrate into the pores of zeolite catalysts can be converted into different substances. Some of these can escape from the pores, but others remain trapped. When this happens, the reaction follows an unexpected path, leading exclusively to the formation of some definite products. Thus, it has been shown[85] that aromatic hydrocarbons are formed in the voids of CaA zeolite, but because of their size they cannot escape from the catalyst crystals and undergo further reactions to give condensation products and carbon. The nature of these products and of the carbon deposits has been investigated[86].

Some examples of the molecular-sieve selectivity of zeolite catalysts, taken from the papers by Minachev and his coworkers[121,122,141], are given in Table 7.

However, the molecular-sieve selectivity of zeolites is not always apparent. For example, the hydration of ethylene oxide (4.2 Å) an NaA zeolite (4 Å) gives ethylene glycol and polyethylene glycol[67]. In this case the pore size does not determine the selectivity, and the reaction takes place on the outer surface of the crystal (in the secondary pore structure). Moreover, the selectivity of zeolite catalysts is not determined exclusively by the relative size of the reactants and the zeolite orifices. According to Borunova and her coworkers[132], a 7.8% Ni/NaX catalyst prepared by ion exchange affords complete hydrogenation of n-octene, whilst benzene is only 5% hydrogenated, in spite of the fact that the hydrogenation of benzene is known[152] to reach 100% on catalysts comprising 4% or more of nickel deposited on carriers.

The zeolite structure can also affect in some cases the reaction mechanism. Thus the channel structure of synthetic mordenite (H form) used as a cracking catalyst is thought[81] to enable reactant molecules to contact several acidic active centres at the same time, which may explain the high isomerisation activity of this material, resulting in a high content of branched hydrocarbons in the cracking products. The long pores in mordenite also favour a more prolonged contact between the reactant and the active surface, resulting in cracking to simpler molecules than with amorphous alumina–silica catalysts.

Thus, geometric factors in catalysis on zeolites combine with the molecular-sieve properties of these materials, which often determine not only whether or not a reaction can occur, but also the nature of the reaction and the type of products formed.

## VI. OPERATING MECHANISM OF ZEOLITE CATALYSTS

Crystalline zeolitic aluminosilicates are similar to amorphous aluminosilicates, and catalyse many reactions which are accelerated by the usual aluminosilicates. The activity of zeolites is often higher than that of aluminosilicates, and increases with the $SiO_2/Al_2O_3$ ratio in the crystal lattice, although the cation-exchange capacity decreases. In natural clays, on the other hand, we find a relation between the cation-exchange capacity and the catalytic activity in cracking reactions[153].

TABLE 7. Selectivity of zeolite catalysts.

| Catalyst | Diameter of orifices in zeolite, Å | Reaction | Conditions | | | Critical diameter of molecules, Å | | Yield of products, % | |
|---|---|---|---|---|---|---|---|---|---|
| | | | temp. | pressure, atm | space velocity, $h^{-1}$ | reactant | product | | |
| 0.5% Pd/CaY | ~8 | isomerisation of n-hexane | 350° | 30 | 1 | 4.9 | 5.6 | isohexanes | 2.4 70.3 |
| 0.5% Pd/CaM | 4–5 | | | | | | | | |
| 0.5% Pd/CaY | ~9 | hydrogenation of benzene | 130° | 30 | 0.5 | 5.8 | 6.1 | cyclohexane | 80 |
| 0.5% Pd/CaM | 4–5 | | | | | | | | 4.2 |
| 0.5% Pd/CaY | ~8 | isomerisation of cyclohexane | 130° | 30 | 0.5 | 6.1 | – | methylcyclohexane | 51.1 |
| 0.5% Pd/CaM | 4–5 | | | | | | | | 2.6 |
| CaY | ~8 | alkylation of benzene by propene* | 250° | 1 | 0.6 | 5.8 | – | cumene + polyisopropylbenzenes | 48.2+19.1 |
| CaM | 4–5 | | | | | | | | 1.3 |
| HM | 6.6 | | | | | | | | 33.1+21.1 |
| CaY ** | ~8 | dehydration of cyclohexanol | 170° | 1 | 3.87 | ~6 | 5.8 | cyclohexene | 100 |
| CaM | 4–5 | | | | | | | | 3 |
| HM | 6.6 | | | | | | | | 100 |
| CaY | ~8 | dehydration of ethanol | 250° | 1 | 3.87 | 4.7 | 4.4 | ethylene | 100 |
| CaM | 4–5 | | | | | | | | 16 |
| HM | 6.6 | | | | | | | | 100 |

* Molar ratio $C_6H_6/C_3H_6$ = 2.5.

** The $SiO_2/Al_2O_3$ ratio in this zeolite was 3.4; in the other cases the ratio was 4.5.

The hydrogen (and decationated) form of a molecular sieve behaves as a solid polymeric acid, and accelerates reactions to which a carbonium-ion mechanism can be assigned. The cationic forms of zeolites, on the other hand, show a different behaviour. Thus, CaX is similar to alumina–silica catalysts in its ability to dealkylate cumene, in its preferential cracking of alkenes as compared with alkanes, and in its tendency to give large amounts of branched hydrocarbons. In contrast, NaX gives cracking products similar to those obtained on pure silica or by thermal cracking. Evidently, the replacement of $Na^+$ by $Ca^{2+}$ ions in a zeolite of a given structure (X) and of constant $SiO_2/Al_2O_3$ ratio brings about a marked change in the properties of the catalyst. It is thought that the reaction follows a radical mechanism on NaX and a carbonium-ion mechanism on CaX.[68] Another experimental fact is the uneven change in activity of the catalysts on increasing the degree of exchange of $Na^+$ in the zeolite by multivalent cations[61,46,121,125,127]. A promoting effect of water and of carbon dioxide on zeolite catalysts has been reported[110,114-116], and also the high stability of these catalysts towards impurity poisons in the crude materials[8,89].

One of the earliest hypotheses aimed at describing the mechanism by which zeolite catalysts operate was put forward by Rabo and his coworkers[46], who suggested that the active centres in zeolites are negatively charged $AlO_4$ tetrahedra. Their conclusion followed from the fact that catalysts based on the decationated form and on the bivalent cationic forms of Y zeolites have identical activities, whereas catalysts based on X zeolites have low activities. On this model, the sodium form of zeolites is inactive in the isomerisation of n-alkanes because the univalent cation fully balances the charge on the $AlO_4^-$ tetrahedron (whatever the $SiO_2/Al_2O_3$ ratio in the zeolite). Replacement of $Na^+$ by $Ca^{2+}$ (i.e. of a univalent by a bivalent cation) in the structure of the X zeolite does not affect the activity of the catalyst because the $Ca^{2+}$ ion is symmetrically located with respect to two neighbouring $AlO_4^-$ tetrahedra, and their negative charges are fully compensated (since the Si/Al ratio in an X zeolite is $\sim 1.2$, i.e. close to unity). In Y zeolites, on the other hand, the Si/Al ratio is twice as large as in type X, and the $Ca^{2+}$ ions are assumed to be located unsymmetrically with respect to neighbouring tetrahedra, so that the binding energy of the cation to one of the $AlO_4^-$ tetrahedra is low. (In planar models the distance between $AlO_4^-$ tetrahedra increases from 2.6 Å to 5.2 Å on passing from zeolite X to zeolite Y.) The result of this dislocation of the bivalent cation is that one of the $AlO_4$ tetrahedra carries a negative charge, which the authors identify with an active centre.

The high activity of zeolites in which $Na^+$ has been replaced by a cation of valency greater than two is explained in a similar way. It is assumed that the isomerisation involves a carbonium-ion mechanism, but how the negatively charged $AlO_4^-$ tetrahedron can induce this reaction is not made clear. As regards the cations in the zeolite, Rabo et al.[46] point to the almost complete lack of catalytic activity in catalysts containing univalent cations and to the very low activity of multivalent cationic forms of zeolites in which the Si/Al ratio is low, i.e. in which the cation density is high, and conclude that these cations contribute little or nothing to the catalytic activity of zeolites. However, this statement conflicts with experimental results showing that in a number of reactions there is a significant difference in the catalytic behaviour of the various cationic forms of zeolites. Furthermore, the possibility of varying the catalytic properties of a given crystal merely by changing the cation was found to be a typical feature of zeolites which is, as Weisz pointed out[68], unique of its kind. The nature of the cation affects the stability as well as the activity of the catalysts[46]. Also, the sodium form of type X zeolites is active in cracking, alcohol dehydration, alkene polymerisation, etc., but CaX zeolite has even greater activity in these reactions. Lastly, the originators of the above hypothesis[46] did not take account of the three-dimensional structure of zeolites, but used a simplified two-dimensional model, which could not provide sufficiently accurate values of the distance between neighbouring $AlO_4^-$ tetrahedra (and therefore also between cations).

Because of all these facts, Pickert, Rabo, and their coworkers subsequently put forward a new model[31] according to which the catalytically active sites in zeolite catalysts are cations having a low degree of coordination to the structural oxygen ions. The activities of various cationic forms of X and Y zeolites were examined in relation to the cracking and the isomerisation of n-hexane and to the cracking of cumene. It was found that the catalytic activity of the zeolite modifications obtained by ion exchange was a function of the charge, size, and environment of the cations. The parts played by the nature of the cations and by the degree of exchange were explained in terms of the lattice structure of zeolites X and Y. In the model for the structure of these zeolites shown in Fig. 2 the solid circles denote two types of cation site, identified by X-ray diffraction analysis of a single crystal of faujasite, which is similar to the synthetic zeolites X and Y.[31] The measured average population of the $S_I$ sites is approximately unity, while that of the $S_{II}$ sites is about one-half. Bivalent cations at sites on an internal surface of the zeolite have only threefold coordination to oxygen ions, whereas at $S_I$ sites between oxygen rings the cations have sixfold coordination to oxygen ions. The charge of a bivalent cation at an $S_I$ site is fully neutralised by the negative charges of the $AlO_4^-$ tetrahedra to which the cation is bound. On the other hand, the charge of a cation at an $S_{II}$ site is only half neutralised. Hence, the electrostatic fields surrounding bivalent cations at the two types of site are different. Calculation shows[31] that the field strength around the cations at $S_{II}$ sites is higher than the value needed to cause considerable shifts in the bonding electrons of the adsorbed molecules. (A field in excess of 1 V $Å^{-1}$ is sufficient to induce a large electronic

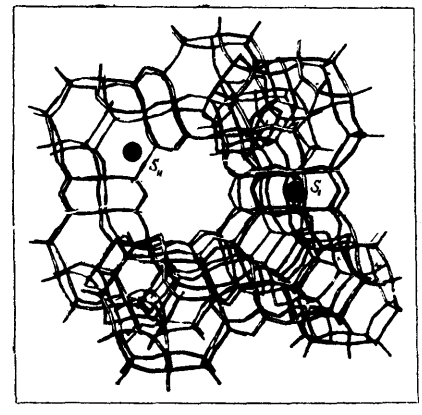



Fig. 2. Structure of the aluminosilicate framework of X and Y zeolite catalysts with two types of cation site.

shift, and in a CaY zeolite the field at these sites is greater than 6 V Å$^{-1}$.) It is suggested that, under the influence of the field of a cation in the zeolite, a C–H bond in an n-alkane molecule becomes polarised in the direction $C^{+}H^{-}$, which leads to the formation of a carbonium ion and to isomerisation[31]. This mechanism does not require physical removal of a hydride ion ($H^{-}$) with formation of an actual carbonium ion. However, the reactivity of the molecules does increase with the field strength.

The non-uniform change in the activity of a zeolite catalyst with degree of exchange of $Na^{+}$ by bivalent (or multivalent) cations is a consequence of the non-equivalence of the cation sites. Cations at $S_I$ sites are the first to undergo ion exchange, and most of these sites become filled with bivalent cations before the latter can begin to replace $Na^{+}$ ions at the catalytically active $S_{II}$ sites. In this way the authors[31] explain why a marked increase in the catalytic activity of a Y zeolite occurs only beyond about the 45–50% level of exchange. With further increase in the degree of exchange the activity of the zeolite catalyst begins to increase faster than linearly.

This model satisfactorily explains most of the experimental results. However, the difference in activity between X and Y zeolites is not convincingly explained, since according to the authors' own calculations the field strength at $S_{II}$ sites in CaX zeolite is lower than in CaY by only 0.7 V Å$^{-1}$. This marginal difference can hardly account for the large difference between the two zeolites, as the authors themselves point out. They consider that, in order to resolve this inconsistency, the model must be refined, and more accurate calculations made, with fewer simplifying assumptions[31].

These views on the nature of the active centres in zeolites attracted a number of objections during the discussion at the Third International Congress on Catalysis[116]. Hirschler suggested that the activity of crystalline zeolites is due to sites akin to Brønsted acid sites, as has been postulated for amorphous alumina–silica catalysts. These sites are due to the presence in the zeolite of water, which is retained even after heating to 500° (see Table 2). This worker notes a similarity in properties between crystalline and amorphous aluminosilicates. Thus, ions of the alkali and alkaline-earth elements deactivate both the hydrogen (or decationated) form of zeolites and amorphous aluminosilicates, the poisoning effect of alkali-metal cations being considerably greater than that of alkaline-earth cations. According to Hirschler[116], the activity of both crystalline and amorphous aluminosilicates varies monotonically with their acidity.

However, important differences in behaviour between zeolites and amorphous alumina–silicas are frequently observed. For example, the hydrogen form of natural mordenite is more similar, as a catalyst, to $AlCl_3$ promoted by HCl than to an amorphous aluminosilicate[83] (see p. 907). Also, there is no direct relationship between the amount of water retained by the zeolite and the catalytic activity. Thus, MgX is less active than MgY towards the cracking of cumene and the isomerisation of alkanes, although it retains a greater proportion of water after being heated to 500° (Table 2). Hence, Rabo et al. believe[31] that the contribution of protonated sites to the carbonium-ion activity of zeolites is insignificant, for the presence of water is interpreted as a potential source of such sites.

According to Plank[116], the rare-earth cationic form of zeolite Y, when dehydrated at 650°, has very low activity towards the cracking of hexane at 204°, but treatment with water increases the activity of the catalyst many thousands of times at the same temperature. He suggests that the activity of the zeolite by water involves the reaction

$$Re^{3+} + H_2O \rightleftarrows Re(OH)^{2+} + H^{+},$$

(where $Re^{3+}$ is a rare-earth cation), the protonated catalyst being the active form, while the salt form is inactive. The present writers[120] have expressed a similar view. The difference in stability between various catalysts based on cationic forms of zeolites X and Y has been explained[116] by the different stabilities of the zeolites HX and HY. The main function of the multivalent cations then consists in controlling the distribution and hence the stability of the acidic ($H^{+}$) sites: the principal difference between crystalline zeolites and amorphous aluminosilicates lies in the geometry of the acidic sites.

We must not ignore the presence of water in zeolites, since its promoting effect on zeolite catalysts is well known (in particular, towards the dehydration of t-butyl alcohol[115]). However, the "hydrolysis" mechanism described above does not appear to be generally applicable. Many experimental facts are difficult to explain from that point of view — e.g. the irregular variation in the activity of zeolites with the degree of exchange of the cations, the considerable activity of univalent cationic forms in certain reactions, etc.

Schwab and Sieb[75] have developed the so-called "two-centre" theory in order to explain the catalytic activity of zeolites. According to this theory, a reaction (such as cracking) can take place only if the catalyst contains, in addition to acidic centres, also negatively charged centres (Lewis bases). The fact that *p*-cymene is converted more readily than is cumene is claimed as evidence in favour of the hypothesis. Indeed, the presence of an electron-donor substituent (the $CH_3$ group) *para* to the isopropyl group causes a significant increase in the total negative charge on the nuclear carbon atom to which the isopropyl group is attached. This may result in a lowering of the activation energy for cracking, irrespective of the particular catalyst used. This theory has not been developed in detail.

Zeolites subjected to isomorphous replacement have given interesting results. Ermolenko and Pansevich-Kolyada[16] have shown that dehydration is the only reaction which ethanol undergoes on NaA zeolite. Deposition of chromic oxide (from potassium chromate) on an industrial NaA zeolite gave a catalyst which again led predominantly to dehydration. Similar behaviour was found with a sample of $Cr(OH)_3$ + NaA, prepared by mixing the zeolite with freshly prepared chromic hydroxide washed free from alkali, although this material contained 15.7% of $Cr_2O_3$. In contrast, a zeolite preparation in which the chromium had been introduced by isomorphous replacement caused the reaction to go mainly in the direction of dehydrogenation, with formation of acetaldehyde. The same behaviour was observed with an amorphous chromosilicate free from aluminium. However, some zeolites with isomorphous replacement, in which the $SiO_2$ content and the total content of $Al_2O_3$ and $Cr_2O_3$ were similar to those in NaA, proved to be catalysts of mixed type and gave approximately equal amounts of hydrogen and ethylene. These results suggest that lattice tetrahedra also can take part in some reactions. Unfortunately, the authors did not examine the behaviour of CrA zeolite prepared by ion exchange: this would have made the situation clearer.

Panchenkov and his coworkers [154] have developed some interesting ideas on the mechanism of the action of aluminosilicate catalysts. They suggest that catalysis on these materials involves reversible changes, under the influence of a reactant molecule, in the coordination of a metal ion in the crystal lattice, from a lower to a higher value. The most active centre is aluminium in fourfold coordination. The greater activity of zeolites may simply be due to the fact that the aluminium is exclusively four-coordinated, whereas in amorphous aluminosilicates the coordination number may vary (4, 5, 6, 8).


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# KINETICS AND MECHANISM OF THE REACTIONS OF ISOCYANATES WITH COMPOUNDS CONTAINING "ACTIVE" HYDROGEN

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## 1. INTRODUCTION

Research workers and technologists have recently been showing great interest in the reactions of isocyanates with alcohols and other compounds containing "active" hydrogen. The reason is that these processes underlie the preparation of several present-day chemical products [1-3].

The reaction of the isocyanate NCO group with an alcoholic hydroxyl is an act of chain propagation in the synthesis of polyurethanes, and has therefore been studied rather more thoroughly than other reactions of isocyanates. In contrast to many known reactions involving nucleophilic addition, however, investigation of the reactions of isocyanates is only in its initial stages.

A few reviews have been published [1,4] on the reactions of isocyanates, but fresh results make it necessary to re-examine several accepted ideas. Furthermore, many aspects of the kinetics and mechanism of these reactions are not yet clear, and demand new quantitative investigations.

## 2. STRUCTURE OF ISOCYANATES AND SOME OF THEIR PROPERTIES

The nature of the reactions undergone by isocyanates and their mechanism are largely determined by the structure of the NCO group and the distribution of electron density in the isocyanate molecule.

The isocyanate group NCO has a linear structure [5-7]. The angle between the R–N and N–C bonds in isocyanates RNCO varies with the nature of the group R. [5-8] There is probably no appreciable conjugation between the R and NCO groups in alkyl isocyanates, as is indicated, for example, by the low energy barrier of 49 ± 3 cal mole$^{-1}$ to rotation of the methyl group in methyl isocyanate [6]. Thermochemical calculations suggest that the conjugation energy in isocyanates is small. According to Pauling [9] it does not exceed 7 kcal mole$^{-1}$ in methyl and ethyl isocyanates. New data on the heats of combustion of isocyanates [10] and on the mean bond energies [11] yield a conjugation energy close to zero for methyl, ethyl, and phenyl isocyanates. This is understandable when it is remembered that the N=C and C=O $\pi$-bonds in the –N=C=O group are formed by carbon by means of $p_y$- and $p_z$-electrons, and are located in perpendicular planes. Nevertheless, the N=C and C=O interatomic distances in methyl isocyanate and isocyanic acid, measured by an electron diffraction method [5], indicate that these bonds are stronger than ordinary double bonds.

Table 1 shows that isocyanates RCNO possess large dipole moments, to which a substantial contribution is made by the NCO group. The fact that the dipole moment decreases† on passing from alkyl isocyanates to HNCO, i.e. with increase in the $R(\delta^+)-N(\delta^-)$ dipole from $\mu_{CN}$ = = 0.61 D to $\mu_{HN}$ = 1.42 D, [15] indicates that the sign of the moment of the NCO group is opposite to that of the R⇌N bond. Hence the nitrogen atom in the NCO group can be assumed to be more negative than the oxygen atom. This view is supported also by the increase in dipole moment on passing from isocyanates to isothiocyanates, which can be interpreted as resulting from replacing the oxygen atom in NCO by the less electronegative sulphur (according to Pauling [9] the electronegativities of oxygen and sulphur are 1.4 and 0.4 eV respectively).

The chemical behaviour of isocyanates agrees most completely with a distribution of charge and electron density in the NCO group represented by conjugation of the valency structures (I)–(III) [6,9]

$$\underset{\text{(II)}}{R-\ddot{\bar{N}}-\bar{C}=\ddot{O}:} \longleftrightarrow \underset{\text{(I)}}{R-N=C=O} \longleftrightarrow \underset{\text{(III)}}{R-\ddot{N}=\overset{+}{C}-\ddot{\bar{O}}:}.$$

TABLE 1. Dipole moments $\mu$ of some isocyanates and isothiocyanates.

| Compound | HNCO | $CH_3NCO$ | $C_2H_5NCO$ | $C_6H_5NCO$ | HNCS | $CH_3NCS$ | $C_2H_5NCS$ | $C_6H_5NCS$ |
|---|---|---|---|---|---|---|---|---|
| $\mu$, D | 1.59 [12] | 2.81 [6] | 2.81 [13] | 2.3 [13] | 1.72 [14] | 3.18 [13] | 3.31 [13] | 3.0 [13] |

† The decrease in the dipole moment of RNCO and RNCS when the alkyl radical is replaced by hydrogen is larger than would follow from vectorial addition of the dipoles [6].