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Catalytic Properties of Zeolites Towards Oxidation Reactions

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We shall review experimental data on the catalytic properties of zeolites towards the oxidation and oxidative dehydrogenation of aliphatic, naphthene, and alkylaromatic hydrocarbons, and of inorganic or organic molecules containing hetero-atoms. The influence of the zeolite structure, of the nature and concentration of the exchangeable cations, and of the valency state of the transition metals on the activity and selectivity of the catalysts will be discussed, together with the effect of these factors on the course of the hydrocarbon oxidation reactions. Specific aspects of the interaction of molecular oxygen and of oxidisable compounds with various zeolites will be examined in the light of ESR, i.r. spectroscopy, and thermal desorption data. We shall show that variations in the structure and composition of the zeolite can lead to different types of reaction, yielding valuable products, and thus confirming the importance of zeolites among oxidation catalysts. 188 references.

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I. INTRODUCTION

Zeolites are salts of solid alumino-silicic acids, characterised by a well defined crystal lattice structure and classified as catalysts of the acidic type. Since the earliest reports of the high catalytic activity of zeolites[1-3] a great deal of work has been done on the acidic properties of zeolites and on their catalytic activity towards reactions of the acid–base type (cracking, isomerisation, alkylation, etc.). Efficient bifunctional catalysts have been developed from zeolites containing Group VIII metals.

One of the least characterised of the zeolite-catalysed reactions of hydrocarbons is their oxidative transformation. The problem is inadequately discussed in the reviews and monographs on zeolites which have been published so far[4-22], and therefore the present review will attempt to deal with various problems in the oxidation of aliphatic, naphthene, and alkylaromatic hydrocarbons, and of H_2, CO, NH_3, H_2S, and alcohols in the presence of zeolites of different composition and structure.

II. OXIDATION OF ALIPHATIC HYDROCARBONS

Though the oxidation of ethylene[23] and of H_2S [24] on zeolites was first reported in 1961, detailed studies of these reactions began only more recently. The deep oxidation†

†This term is used throughout the paper to denote total oxidation to CO_2 and H_2O.

of methane on type X zeolites containing various transition metal cations has been investigated[25,26], and the reaction on iridium-, rhodium-, and palladium-containing zeolites has been shown to be kinetically of first order with respect to methane and of zero order with respect to oxygen[25]. On a Pt-containing X-type zeolite the reaction has a negative order with respect to oxygen, suggesting competitive adsorption of methane and oxygen. The correlation between the activity of the zeolite and the coordination number of the transition metal cation has been stressed[26]. The activation energy of the reaction on Pd-containing type X zeolites prepared by steeping and by ion exchange methods is 50 and 88 kcal $mole^{-1}$ respectively, indicating a large difference in the catalytic properties towards the deep oxidation of methane between metallic palladium and the palladium cations in a zeolite lattice.

The oxidation of ethylene on type Y zeolite containing transition metal cations is discussed in Refs. 27 and 28. Deep oxidation of ethylene, with formation of CO_2 and H_2O, was observed on all the samples. The most active catalysts are Cu(II)Y and Cr(III)Y, and the least active are Ni(II)Y and Mn(II)Y, the latter being almost indistinguishable from the initial NaY zeolite in catalytic activity. The possibility of participation in the reaction by the oxygen atoms of the catalysts themselves was tested by first treating the zeolites with oxygen and then admitting the ethylene as a series of separate pulses. The presence of active oxygen in the zeolite is inferred from the appearance of peaks of reaction products in the chromatograms. The amount of reaction oxygen stored in the sample depends on the nature of the ion-exchange cation. With the least active [Ni(II)Y and Mn(II)Y] samples the amount of oxidation products detected in the chromatograms is very small, whereas on Cu(II)Y zeolite the amount of active oxygen increases steeply with the oxygen pre-treatment temperature.

The catalytic activity of type Y zeolite and the amount of reactive oxygen held by the catalyst have been shown[29] to vary non-linearly with the degree of exchange of sodium by copper cations, suggesting non-equivalence of the copper localisation sites in the zeolite lattice. Activated adsorption of ethylene in the pre-catalytic region has been demonstrated. At lower temperatures physisorption takes place, and the degree of exchange of sodium by copper ions has no effect on the heat of adsorption of ethylene. After removal of the active oxygen from CuY zeolites the adsorption of ethylene is markedly enhanced, possibly as a result of a strong direct bond between ethylene and the copper ion. Substantial adsorption of ethylene on Cu(I)Y and Ag(I)Y zeolites with formation of π-complexes has been detected[30] by i.r. spectroscopy. With the Cu(II)Y, Zn(II)Y, and CaY zeolites the main contribution to the interaction with ethylene is from van der Waals forces. The heat of adsorption of ethylene on Cu(I)Y is 15.9 kcal $mole^{-1}$, but only 9.5 kcal $mole^{-1}$ on Cu(II)Y.

An oxidation reaction of ethylene of great practical importance is the preparation of ethylene oxide. A method of producing ethylene oxide by using zeolite catalysts was patented[23] in 1961, but a detailed study of this reaction on type A and X zeolites in the presence of ionic silver was only recently reported[31]. Samples prepared by ion exchange were shown to have a low selectivity towards ethylene oxide at 200–300 °C, whereas the catalysts prepared by steeping the initial zeolite offer both a high activity and a high selectivity in this reaction. The most selective catalyst is Ag–CaA, the yield of ethylene oxide and the selectivity of the reaction increasing in proportion to the amount of silver and reaching levels of 25 and 70% respectively on a 30% Ag–CaA catalyst at 250 °C.

The oxidation of ethylene on type Y zeolite containing both copper and palladium cations has been shown[32–35] to give acetaldehyde in the presence of water vapour. In isolation, neither Pd(II)Y nor Cu(II)Y is an active catalyst; the activity of a sample prepared by adding first 4 wt.% of Cu and then 1 wt.% of Pd is twice as high as that of a catalyst containing the same amounts of Cu and Pd but added in the reverse order[32].

The activity of PdCu catalysts towards the oxidation of ethylene and propylene is markedly dependent on the crystal structure of the zeolite[33]. In particular, the X and Y zeolites with large pores are more active towards the formation of acetaldehyde than type A and mordenite type zeolites. It appears that the reaction takes place mainly in the zeolite lattice holes, and the contribution to the total activity from centres located on the outer surface of the crystal is small. It is stressed[33] that samples prepared by steeping are often superior to ion-exchanged forms of zeolite in both activity and selectivity.

The highest activity towards the oxidation of ethylene to acetaldehyde is found[34,35] in type Y zeolite containing 6 wt.% of copper and 1.5 wt.% of palladium. The optimum oxidative regeneration temperature of these samples was found to be 300°.

Several workers[36–42] have studied the oxidation of propylene on zeolites containing exchangeable transition metal cations. In the presence of type Y zeolite in which the sodium cations have been replaced by copper the main reaction at 350° is deep oxidation of propylene[36]. Small amounts of formaldehyde, acrolein, and acetaldehyde are also formed. A comparison of the activity of Cu(II)Y with that of CuO supported on SiO_2 has shown that the rate of oxidation of propylene on the zeolite can be an order of magnitude greater than on CuO/SiO_2: according to Mochida and coworkers[36] this is due to a specific state of the copper ions on the surface of crystalline aluminosilicates. The activity of Cu(II)Y towards the oxidation of propylene was found to be greater than towards the oxidation of ethylene.

The oxidation of propylene in the presence of water vapour at 300° gives a high yield of acrolein [up to ~7% on Cu(II)Y zeolite if the reaction mixture contains 30–50 vol.% of water vapour[37]]. On Ag(I)Y zeolite under otherwise similar conditions the yield of acrolein is less than 3%, and on Ni(II)Y no acrolein can be detected in general. At 200° isopropanol formation is detected, in keeping with the acidic function of the zeolite.

Increasing the $C_3H_6:O_2:H_2O$ molar ratio in the reaction mixture to 1:1:20 gives acetaldehyde at 250° and acetone at temperatures above 500°.[38] It is pointed out[39] that in order to obtain equal concentrations of acrolein and carbon dioxide in the reaction products the $C_3H_6:O_2$ ratio must be increased to 1:7, and the temperature must be raised to 350°.

In the liquid phase propylene dissolved in benzene is converted into propylene oxide with a selectivity of 70% in the presence of NaX zeolite steeped in ammonium molybdate and of oxygen (150 °C, 45 atm).[40] In a study[41] of the oxidation of propylene on type X zeolites containing Pd, Cu, Co, Ni, Zn, Mn, Cr, Fe, and NH_4 cations the main reaction products were found to be CO_2 and H_2O, with small amounts of acrolein, formaldehyde, and acetaldehyde. The activity of the samples increased with their acidity, but the addition of pyridine to the reaction mixture lowered the activity of the catalysts. From these results the authors concluded[41] that the reaction mechanism is

$$CH_3{-}CH{=}CH_2 + H^+ \rightarrow CH_3{-}C^+H{-}CH_3$$
$$CH_3{-}C^+H{-}CH_3 + (Cu\ldots O_2)^+ \rightarrow CH_3{-}C^+H{-}CHO + H_2O + Cu^+$$
$$CH_3{-}C^+H{-}CHO \rightarrow CH_2{=}CH{-}CHO + H^+ .$$

The intermediate products are further oxidised with formation of CO_2 and H_2O.

Iron-containing zeolites of types A, X, and Y also are active exclusively towards the deep oxidation of propylene[42]. The addition of Fe(III) to X and Y zeolites increases their activity slightly, but in type A zeolite the effect is not detected.

The oxidation of propylene on VONaY zeolite, prepared by ion exchange between NaY zeolite and an aqueous solution of vanadyl sulphate, gives mainly CO_2, acetone, and acetaldehyde[43]. Supported catalysts (V_2O_3/SiO_2) are less active than VONaY towards the oxidation of propylene. It is suggested[43] that this reaction gives only partial oxidation, whose products undergo polymerisation or carbonisation and remain in the internal cavities of the zeolite structure.

The addition of ammonia to the reaction mixture used in the oxidation of propylene leads to oxidative ammonolysis, with formation of acrylonitrile. The activity of the catalysts depends on the structure of the zeolite and on the coordination of the transition metal ions in the zeolite matrix. A study[44] of the activity of Fe(III)-containing zeolites towards this reaction has shown that the yield of acrylonitrile decreases in the sequence FeNaX > FeNaY > FeNaA. The low activity of type A zeolite as compared with the faujasites obviously stems from special features of this type of zeolite skeleton. The most selective catalysts with respect to the formation of acrylonitrile are FeNaX, FeCaX, and FeCaA, whereas FeNaY is the most active towards the formation of CO_2.

The oxidative ammonolysis of propylene has been studied[45] on Fe(II)Y and Fe(II)-mordenite zeolites. At 450° the conversion of propylene on Fe(II)Y was only 17% (10% CO_2, 7% acrolein, acrylonitrile not detected), but in the presence of the Fe(II)-mordenite catalyst the yield of acrylonitrile is as high as 40% for a total conversion of 43%. These results illustrate the important effect of the zeolite structure on the activity and selectivity of the catalyst. Using γ-resonance spectroscopy data Garter and coworkers[45] ascribe this difference between the Fe forms of type Y and mordenite zeolites to the oxidation state and to the location of the iron ions in the two materials.

In the oxidative ammonolysis of propylene and of the butylenes the Mn form of type X zeolite shows a selectivity higher than those of MnY and Mn-erionite zeolites[46], which are more effective as cracking catalysts. It has been pointed out[47] that on NaX zeolite containing 10% Ag_2O the yield of acrylonitrile is 35.5%, whereas gumbrin containing the same amount of silver is more active and selective towards the formation of acrolein.

The interaction of butenes adsorbed on CaA and NaX zeolites with oxygen at 25–90° has been studied[48]. The resulting complex mixture of products can be separated from the zeolites only by extraction with moist ether. This very strong interaction between the zeolites and organic molecules is due to the similarity between the pore size and the molecular diameters. The effect is most clearly seen when the products are more polar than the initial hydrocarbons. After analysing the reaction products the authors[48] conclude that catalytic oxidation on zeolites causes preferential breaking of the double bond.

The Pt–NaA zeolite was found[49,50] to have a high activity towards the oxidation of CO. When a mixture of air and CO (2 mole %) is passed through the catalyst at 427–540° the degree of conversion of CO is 86–100%. Under the same conditions the conversion of n-butane is only 2.4–5.5%.[49] The Pt–CaA zeolite containing 0.3 wt.% Pt has a high selectivity towards the oxidation of n-paraffins and n-olefins mixed with iso-paraffins and iso-olefins. Thus, 97% of the n-butane and only 0.1% of the isobutane are oxidised to CO_2 and H_2O from a 6:4 mixture of the two compounds at 315°. On the same catalyst propylene and but-2-ene are oxidised fully and selectively in the presence of isobutane. Thus, these systems show the molecular sieve effect.

One of the earliest studies of the deep oxidation of hydrocarbons was on zeolites not containing transition metals[51]. The activities of NaX, CaX, and MnX zeolites towards the oxidation of hexane isomers were compared, and MnX (i.e. a zeolite containing cations of a typical transition metal) was found to be inferior to NaX zeolite in its activity towards deep oxidation. The catalysts were placed in the following series with respect to the extent of carbon formation: CaX > MnX > NaX. The authors[51] point out that the zeolite reaction does not correspond to the typical oxidation–reduction mechanism of transition metal oxides, since NaX is more active than MnX. Gradual replacement of the sodium by bivalent cations suppresses the oxidative activity, and the cracking reaction becomes predominant.

Recent scientific papers and patent applications highlight the high activity of zeolites towards the oxidation of various substances. Thus, Doronina and coworkers[52] studied the catalytic behaviour of the zeolites NaA, NaX, NaY, PdY, NiY, CoY, Pd-mordenite, and Tseokar-2 towards the deep oxidation of chlorinated organic compounds. At 400–450° over 90% oxidation was obtained on NaY, PdY, CoY, and Pd-mordenite. Selective oxidation of hexafluoropropylene takes place on catalysts consisting of NaY zeolite in which the Na atoms have been replaced by Cr, Mn, Fe, Ni, Pd, or Ce ions to an extent greater than 50 equiv.%.[53] A substantial level of activity towards this reaction was obtained also with samples prepared by steeping NaY zeolite and amorphous alumina–silica in an aqueous solution of copper nitrate[53,54]: the extent of conversion was 15.0 to 29.1% at 250–300°, with a selectivity of 45.1–47.7%. A high activity towards the deep oxidation of carbon compounds at relatively low temperatures (<150°) has been observed with synthetic zeolites steeped in a solution of $H_2PtCl_6 \cdot 6H_2O$ in an organic solvent[55] and with ZSM-5 zeolite containing copper cations[56]. The increasing number of publications on the deep oxidation of various compounds in the presence of zeolite catalysts shows the importance of this topic.

We may conclude from published results that low-molecular-weight hydrocarbons on the whole undergo deep oxidation on zeolites, those containing transition-metal cations usually being the most active. As the molecular weight of the hydrocarbon increases, oxidative dehydrogenation may occur in parallel with the deep oxidation, but this phenomenon has not been studied extensively so far. Thus, Al'tshuler and Tsitovskaya[57] suggested the following method of preparing catalysts for the oxidative dehydrogenation of paraffins in the presence of halogens: a sample of Na-mordenite zeolite is steeped in an aqueous solution of H_2PtCl_6, dried at 140°, baked in air at 380°, and reduced in hydrogen at the same temperature. The sodium cations are then exchanged by caesium cations. In the presence of this catalyst the conversion of n-butane is 37.1%, with a selectivity of 79.2% towards butylenes and divinyl, for a mixture of reactants in the molar ratio n-butane : O_2 : Br_2 = 1:2:0.7.

In a study of the oxidative dehydrogenation of isopentane on zeolite catalysts[58,59] the conversion of isopentane on CaA, CaX, and CaY at 540° and a molar ratio iso-C_5H_{12} : O_2 = 1:1.8 was found to increase with the pore size of the zeolite, but the selectivity of the process was low[58]. In the case of type A zeolite containing Fe(III), Cr(III), Co(III), or

Zn(II) cations a direct relationship is observed between the extent of conversion of isopentane and the ionic radius of cations with the same charge[59]. The selectivity of the reaction towards isopentylenes and isoprene is not greater than 26%.

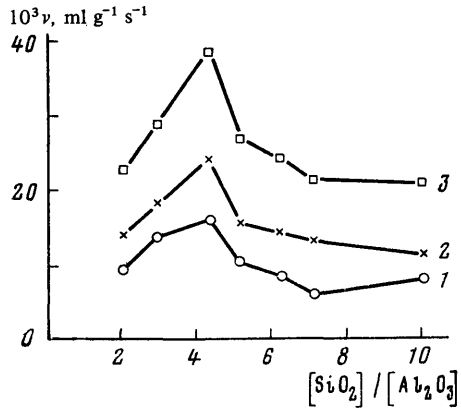


Figure 1. Rate of oxidative dehydrogenation of 2-methylbut-2-ene against the $[SiO_2]/[Al_2O_3]$ ratio in zeolite at: *1*) 400, *2*) 425, and *3*) 450 °C (Ref.60).

A study[60] of the effect of the composition and structure of the zeolites on the oxidative hydrogenation of 2-methylbut-2-ene showed that, in addition to oxidative dehydrogenation, zeolite catalysts can induce deep oxidation, isomerisation of the double bond, and cracking reactions. The yield of isoprene and the selectivity of the process are particularly sensitive to the zeolite structure. A comparison of the activities of the Na forms of A, X, and Y synthetic zeolites, chabazite, erionite L, and mordenite showed that the reaction rate goes through a maximum (corresponding to type Y zeolite) as the ratio of silicon to aluminium oxides is varied (see Fig.1). The apparent activation energy for Na-faujasite is ~15 kcal $mole^{-1}$, increasing to 18–20 kcal $mole^{-1}$ for type A zeolites, chabazite, erionite, and mordenite. The faujasites are superior to the narrow-pore zeolites in the yield of isoprene and in the selectivity of the process, but the latter are more active towards deep oxidation. In other words, X and Y zeolites behave differently from zeolites with narrow pores towards the oxidative dehydrogenation of 2-methylbut-2-ene.

The interaction of 2-methylbut-2-ene with different zeolites has been studied also by programmed thermo-desorption[61]. The thermo-desorption spectra of X, Y, and L zeolites were found to include three peaks (at 75–80, 130–170, and 200–300° respectively), though the adsorption capacity of faujasites for this compound is much greater than that of type L zeolites. With chabazite and erionite only one desorption peak is observed (t_{max} = 125–150°), and with type A zeolite two peaks with t_{max} at 150–160 and 300–350° respectively (Fig.2). This difference in the interaction of 2-methylbut-2-ene with different Na-zeolites accounts for the difference in activity and selectivity between faujasites and narrow-pore zeolites.

The effect of the nature of the exchangeable cation in type Y zeolite on the oxidative dehydrogenation of 2-methylbut-2-ene has also been studied[60]: as the ionic radius increases in the sequence Li < Na < K < Rb the yield of isoprene and the selectivity of the reaction decrease, and the yield of carbon oxides increases. At 400–450° a linear decrease of the reaction rate with increase of the ionic radius of the alkali metal cation is observed. It may be due to variations in the electrostatic field within the zeolite holes, or alternatively it may be due to the blocking effect of the larger cations on the "windows" leading to the large zeolite holes, which could hinder the diffusion of hydrocarbon molecules.

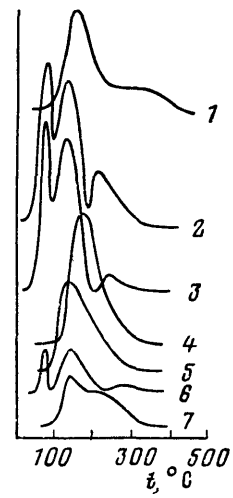


Figure 2. Thermo-desorption spectra of 2-methylbut-2-ene on zeolites: *1*) NaA, *2*) NaX, *3*) NaY, *4*) Na-chabazite, *5*) Na-erionite, *6*) NaL, *7*) Na-mordenite (Ref.61).

III. OXIDATIVE TRANSFORMATIONS OF NAPHTHENES

The oxidation of cyclohexane on zeolite catalysts has been studied in detail in the Soviet Union and in Japan. Using type Y zeolites containing copper cations the main products were found[62] to be benzene, CO_2, and H_2O. Cu(II)Y zeolite is more active than the conventional catalyst for this reaction (CuO on silica gel). For conversions up to 10% the selectivity of the reaction with respect to benzene can be as high as 80%. In addition to the Cu(II) form, type Y zeolites containing Pd(II), Ag(I), Zn(II), Ni(II), and Cr(III) were also investigated. Cu(II)Y was found to be the most active in the formation of benzene, and Pd(II)Y in the deep oxidation reaction. The authors point out[62] that the most active catalysts have the highest activation energies and frequency factors. The dependence of the initial rates of formation of benzene and of carbon dioxide on the standard heat of formation of the metal oxide is described by curves with two peaks[63]. Similar relationships are observed for the dehydrogenation of cyclohexane to benzene on oxide catalysts[64,65], but in this case the activity maximum corresponds to the catalyst Cr_2O_3.

NaY zeolite was found[66,67] to be active only towards the deep oxidation of cyclohexane (which sets in at temperatures as low as 150–160°). In contrast to the reaction on NaY, the oxidation of cyclohexane on the Cu(II) and Fe(III) forms of type Y zeolite begins at 240–260°, and proceeds

in two directions: deep oxidation, and oxidative dehydrogenation to benzene. As the degree of exchange of the sodium cations by transition metal cations is increased, the yield of benzene increases, but the specific activity of the catalyst [expressed for one Cu(II) or Fe(III) ion] decreases. The selectivity of the reaction towards benzene and the concentration of mobile oxygen in the zeolite increase with the exchange of sodium cations by transition metal cations. Mobile oxygen atoms are absent in Mn(II)Y, Co(III)Y, and Zn(II)Y zeolites: these materials behave like NaY zeolite, giving only deep oxidation products. On the other hand the zeolites containing Cu(II), Fe(III), Cr(III), and Ni(II) cations (active towards the oxidative dehydrogenation of cyclohexane) contain "active" oxygen. It has been pointed out[66,67] that the selectivity of the benzene formation reaction is higher in crystalline alumina–silicas containing transition metal ions than in the amorphous catalysts containing the same transition metals.

Spectral studies by the pulse method[68] have demonstrated the strong adsorption of cyclohexane on NaY zeolite in the pre-catalytic temperature region. After exposure to a $C_6H_{12} + O_2$ mixture, even at 60–80°, NaY zeolite shows characteristic absorption bands at 1720, 1780, and 1820 cm^{-2} (corresponding to carbonyl and peroxide compounds). After partial replacement of the sodium ions by Cu(II) these compounds are no longer observed (up to 180°).

An interesting feature of the deep oxidation of cyclohexane on NaX and NaY zeolites in the development of an oscillatory (autocatalytic) oxidation regime, ascribed[68,69] to periodic increases in the concentration of peroxide compounds on the zeolite surface. By studying the effect of temperature on this process it was shown that the oxidation of cyclohexane on Na faujasites has a mixed (homogeneous–heterogeneous) mechanism[68–70]. The penetration of the reaction into the gas phase occurs at 120° in the case of NaY, and at 220° in the case of zeolites containing transition metals. According to Elinek and coworkers[70] the relative extent of the homogeneous reaction exceeds 60% when the reaction mixture contains 0.3–0.6 vol.% of cyclohexane.

By applying thermo-desorption and calorimetry methods to the cyclohexane–NaX system it was shown[71] that cyclohexane is adsorbed in one form only, with an activation energy for desorption of 18 kcal $mole^{-1}$ in a stream of helium and 13 kcal $mole^{-1}$ in air. In both cases the adsorption is reversible, and almost the whole of the adsorbed cyclohexane is evolved during the desorption. This excludes any mechanism which explains the oscillatory regime (i.e. periodic changes in extent of conversion and in temperature) by postulating several forms of adsorbed cyclohexane. The heat of adsorption of the cyclohexane is independent of the surface coverage of the catalyst, showing that the surface is energetically uniform towards cyclohexane, and allowing the dependence of the activation energy of one of the steps on the coverage of the surface by the reactant to be rejected as an explanation of the oscillations occurring during the oxidation of cyclohexane. On the basis of these results the authors suggest[71] that when cyclohexane and oxygen are added sequentially peroxide compounds are formed by the reaction of cyclohexane with the free radical forms of adsorbed oxygen, further oxidation involving oxygen from the gas phase. The marked dependence of the reaction rate on the concentration of oxygen in the reaction mixture is interpreted[72] as evidence for the participation of oxygen in the chain propagation reactions.

The kinetics of the oxidative dehydrogenation of cyclohexane on Cu(II)Y zeolite were studied by Elinek and coworkers[73]. The rates of oxidative dehydrogenation and of deep oxidation of cyclohexane were found to depend on the partial pressures of the reactants according to the equations

$$v(\text{benzene}) = k \cdot p_{O_2}$$

$$v(CO_2) = k' \cdot p_{O_2}^{0.5} .$$

Thus the rates of both reactions are practically independent of the partial pressure of cyclohexane.

By studying the adsorption of oxygen and cyclohexane on the catalysts by the chromatographic pulse method, with the reactants introduced in different orders, the adsorption of oxygen was found to be rate-determining in the oxidative dehydrogenation of cyclohexane to give benzene. The high yields of benzene in the presence of Cu(II)Y are due to the high adsorption capacity of this zeolite towards oxygen. The rates of deep oxidation and of oxidative dehydrogenation of cyclohexane at 290° are given in Table 1, together with the adsorption capacities of various cationic forms of type Y zeolite towards cyclohexane and oxygen[73]. For low degrees of exchange of sodium by copper cations the reaction products contain only a small amount of cyclohexane (<1%), and on the samples with a high Cu(II) content no cyclohexane can be detected. According to these results the authors[73] propose the following scheme for the transformations of cyclohexane on zeolites:

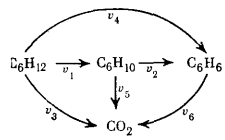


Table 1. Catalytic activity (α) and adsorption capacity (γ) of the cationic forms of type Y zeolite[73].

Catalysts	$10^2 \alpha$*, ml g^{-1} min^{-1}		γ**	
	$v(C_6H_6)$	$v(CO_2)$	C_6H_{12}	O_2
Cu (II) Y	52.0	22.0	100	100
Pd (II) Y	4.4	7250.0	200	<1***
Cr (III) Y	2.3	9.6	<1	<1
Zn (II) Y	0.4	3.2	<1	<1
Ni (II) Y	1.4	7.3	<1	<1
Ag (I) Y	0.2	2.5	<1	<1

*Rate of the reaction at 290°.

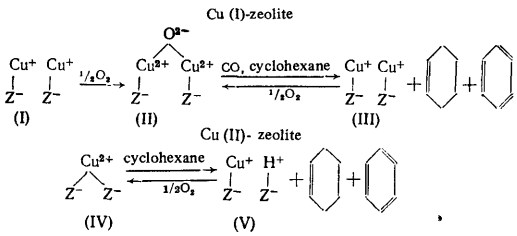
**The adsorption capacity of Cu(II)Y zeolite is arbitrarily taken as 100.

***On Pd(II)Y benzene is formed by dehydrogenation of cyclohexane without involving oxygen.

The oxidation of cyclohexane, ethylene, and CO on type Y zeolites containing Fe(III), Fe(II), Cu(II), and Cu(I) cations has been studied[74], and the Cu(I)Y and Fe(II)Y zeolites were found to be catalytically more active towards the oxidation of CO than Cu(II)Y and Fe(III)Y zeolites. This is explained in terms of the amount of oxygen chemisorbed on the catalyst [negligibly small in the case of catalysts containing Cu(II) and Fe(III) ions]. A further increase in the valency of these ions is energetically very difficult, whereas oxygen chemisorption on zeolites containing Cu(I) and Fe(II) can readily take place, to give a 0.44–0.5 ratio of the numbers of oxygen atoms and metal ions. The authors[74] point out that Cu(II) zeolite has a small but measurable

activity although oxygen adsorption on this material is undetectable, and they explain this observation by postulating activation of the oxygen in the zeolite structure by the added copper.

In contrast to the oxidation of CO, in the oxidative dehydrogenation of cyclohexane no difference was found between the catalytic activities of Cu(II)Y and Cu(I)Y [or Fe(III)Y and Fe(II)Y]. The behaviour of the system is explained[74] by postulating the following reaction schemes for Cu(I) and Cu(II) zeolites:



In these equations Z^- is the anionic form of the zeolite. In the oxidation of CO, which requires the presence of active O^{2-}, the preferred structure is (II). However, in the dehydrogenation of cyclohexane structures (II) and (IV) have equal activities. An analogous mechanism can be written for Fe(II) and Fe(III) zeolites.

The selectivity of the formation of benzene by the oxidative dehydrogenation of cyclohexane on Cu(I)Y, Cu(II)Y, Cu(II)-mordenite, and CuO/SiO_2 catalysts was found[75] to be 83, 76, 0.44, and 33% respectively, with activation energies of 27, 18, 38, and 20 kcal $mole^{-1}$. The kinetic order of the reaction with respect to oxygen was 1 on Cu(II)Y zeolite and 0.5 on Cu(I)Y. Cyclopentane on these catalysts undergoes mainly deep oxidation: whereas in the presence of Cu(I)Y the rate of oxidation of cyclohexane is almost an order of magnitude greater than that of cyclopentane, in the presence of Cu(II)Y the two rates are almost equal. Furthermore, the activity of Cu(I) towards the oxidation of cyclopentane rapidly decays with time, whereas the activity of Cu(II)Y is relatively stable. These differences between the catalytic properties of copper-containing zeolites are explained[75] by postulating the participation of O_2 in the oxidation on Cu(II)Y and of dissociatively adsorbed oxygen in the oxidation on Cu(I)Y.

The dehydrogenation of cyclohexane on various cationic forms of type X zeolite has been studied[76-78] both in the presence and in the absence of oxygen. Na-, Ca-, and decationated forms were found to be practically inactive towards the formation of benzene, but the introduction of nickel cations creates dehydrogenation activity which increases with the amount of nickel added to the sample. In the presence of oxygen the Ni-containing zeolites are active also in the oxidative dehydrogenation with formation of benzene, whereas the activity of NaX is high only towards deep oxidation. As the amount of sodium in the zeolite decreases the extent of the deep oxidation reaction also decreases very markedly. The most active and selective catalyst for the formation of benzene is a sample in which 25% of the sodium has been exchanged by nickel cations and 33% by hydrogen ions.

An interesting feature of the Fe(II) form of type Y zeolite has been pointed out[79]: the production of cyclohexene by the oxidative degradation of cyclohexane. In a pulsed regime at 180° the conversion of cyclohexane is 2.5%, with 58% selectivity for cyclohexene. The Co(II)Y, Cu(II)Y, and Cr(III)Y zeolites show a lower activity and selectivity for the formation of cyclohexene. Increasing the partial pressure of oxygen in the reaction mixture and the contact time increases the conversion, but it lowers the selectivity for cyclohexene. On Fe(II)X zeolite, and in the presence of water vapour, the conversion of cyclohexane at 260° is 14%, and the selectivity for cyclohexene is 30%.[80] The Fe-mordenite catalyst shows no activity towards the formation of cyclohexene up to 430°. Thus, the activity of iron-containing zeolites towards the formation of cyclohexene decreases in the sequence FeX > FeY > Fe-mordenite. Kubo and coworkers[80] suggested, in the light of published results[81-83], that dissociatively adsorbed oxygen [detected by γ-resonance spectroscopy on Fe(II) zeolites] plays an important role in this reaction on low-valency cationic forms of faujasite.

Later work on the oxidation of cyclohexane on crystalline aluminosilicates showed that the direction of the reaction is also strongly influenced by the structure of the zeolite. Thus, whereas faujasites catalyse the reaction (depending on the nature of the exchanged cation) towards deep oxidation of the cyclohexane or towards oxidative dehydrogenation with formation of benzene, in the case of the alkali metal forms of synthetic type A zeolites and of sodalite, chabazite, erionite, and mordenite the oxidative dehydrogenation of cyclohexane stops at the cyclohexene stage[84-91]. On the more active catalysts the yield of cyclohexene is greater than 20%, which is almost 5–10 times greater than the activity of Fe(II)-containing faujasites. Table 2 shows some results on the activity and selectivity of zeolite catalysts towards the oxidative dehydrogenation of cyclohexane to cyclohexene[85-88]. The tabulated values show that the introduction of transition metal cations (Pd, Cu, Fe) into the zeolite composition lowers the selectivity for this reaction (in comparison to the alkali metal cation forms). Thus, in contrast to the Na faujasites (which are active only towards deep oxidation), the Na forms of narrow-pore zeolites cannot accommodate the cyclohexane molecules in the internal zeolite holes, and on these catalysts the oxidative dehydrogenation stops at the stage of cyclohexene formation.

Table 2. Oxidative dehydrogenation of cyclohexane on zeolites (molar ratio $C_6H_{12}:O_2 = 1:1.5$; $V = 1\ h^{-1}$)*.[88]

Zeolite	$[SiO_2]/[Al_2O_3]$	t, °C	Conversion, %	$W_{C_6H_{10}}$, %	S, %
NaA	2.0	400	25.6	18.3	71
Na-sodalite	2.0	400	23.1	16.0	69
Na, K-chabazite	5.1	450	28.3	20.5	73
0.08Pd-chabazite	5.1	450	26.1	18.3	70
Na, K-erionite	6.2	450	25.3	19.2	76
0.08Pd-erionite	6.2	450	33.6	20.9	62
0.25Fe-erionite	6.2	450	28.5	18.3	64
0.30Cu-erionite	6.2	450	20.0	13.5	67
Na, K-L	7.1	400	15.2	12.3	81
Na-mordenite	10.0	400	16.3	13.4	82
0.08Pd-mordenite	10.0	400	17.2	14.4	78
Clinoptilolite**	~10	400	20.2	16.1	80

*Symbols: V is the volume velocity for cyclohexane, $W_{C_6H_{10}}$ is the yield of cyclohexene, S is the selectivity of the reaction.

**Molar ratio $C_6H_{12}:O_2 = 1:1$, $V = 0.5\ h^{-1}$.

A study of the interaction of cyclohexane with various zeolites by the thermo-desorption method[89] has shown that cyclohexane is adsorbed only on type X and Y zeolites, and to a smaller extent on type L zeolite. Hence it was suggested that the strong adsorption on faujasites is responsible for the deep oxidation of cyclohexane on zeolites.

But although L type zeolite adsorbs cyclohexane, its adsorption capacity is very low. This may be the reason for the low yield of cyclohexene (as compared with other narrow-pore zeolites) of this catalyst, which occupies a position intermediate between the narrow-pore catalysts and the faujasites.

The t_{max} value of the cyclohexane desorption peak on different cationic forms of zeolite Y is displaced towards lower temperatures as the initial NaY zeolite is converted into the working form: in other words, the strength of the adsorbate–adsorbent bond is lowered, and the effective diffusion coefficient increases almost by two orders of magnitude[89]. These changes affect the catalytic properties of the samples. Unlike NaY, which catalyses only the deep oxidation of cyclohexane, NdY catalyses the oxidative dehydrogenation of this compound to give benzene. On the other hand, with narrow-pore zeolites (which do not, in general, adsorb cyclohexane) the main product is cyclohexene.

The kinetics of the oxidative dehydrogenation of cyclohexane in the presence of Na, K-erionite have been studied in our laboratory[88]. The reaction is first-order in oxygen, and has a fractional order with respect to cyclohexane. The apparent activation energy is only 5.5 kcal mole^{-1}. The rate-limiting step is assumed to be the surface reaction between cyclohexane and the weakly adsorbed molecular oxygen. The experimental results are satisfactorily described by the equation

$$v = \frac{k \cdot p_{O_2} p_{C_6H_{12}}}{1 + a_{C_6H_{12}} p_{C_6H_{12}}},$$

where $a_{C_6H_{12}}$ is the adsorption coefficient of cyclohexane.

Table 3. Oxidative dehydrogenation of cyclohexene on zeolites (450 °C, $C_6H_{10}:O_2 = 1:1$, $V = 1\ h^{-1}$).[88]

Zeolite	Conversion, %	W, %		S, %	
		C_6H_8	C_6H_6	C_6H_8	C_6H_6
Na	7.3	2.9	3.9	38	53
Na, K-chabazite	16.1	7.7	7.7	48	48
0.08Pd-chabazite	9.1	3.3	5.4	36	59
Na, K-erionite	8.3	3.4	3.4	41	41
0.08Pd-erionite	10.2	1.4	7.2	14	71
0.25Fe-erionite	11.9	1.3	7.1	11	60
0.30Cu-erionite	11.4	0.8	6.2	7	54
Na, K-L	6.7	2.4	3.3	36	49
Na-mordenite	10.4	3.3	4.2	32	40
0.08Pd-mordenite	10.0	2.3	5.5	23	50

Since the oxidative dehydrogenation of cyclohexane on narrow-pore zeolites stops at the cyclohexene formation stage, we examined[88] the possibility of preparing cyclohexadiene by the oxidative dehydrogenation of cyclohexene. The results (Table 3) show that (except in the case of Na, K-chabazite sample) the yield of cyclohexadiene is 3.4% or less, and the selectivity of the reaction varies between 7 and 48%. An increase in temperature or in the oxygen to cyclohexene concentration ratio favours the yield of benzene and thus lowers the selectivity for cyclohexadiene. The introduction of transition-metal cations into the zeolite also results in a lower selectivity.

We have also studied[90] the oxidative dehydrogenation of cyclohexane on natural zeolites (thomsonite, stilbite, natrolite, analcite, lomontite, mordenite, heulandite, and clinoptilolite). On all these samples the reaction was found to yield mainly cyclohexene: the highest activity was observed with a zeolite sample of the thomsonite type, which gave a 20.8% yield of cyclohexene at 450° with a selectivity of 80%. The zeolite structure has a marked effect on the temperature dependence of the yield of cyclohexene (Fig.3). In some cases the yield goes through a maximum at 400° (clinoptilolite and heulandite), whereas with thomsonite the yield continues to increase with temperature up to 450°. However, at still higher temperatures the selectivity decreases in every case.

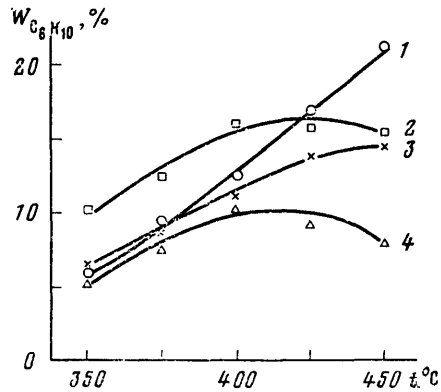


Figure 3. Yield of cyclohexene against temperature for natural zeolite types: *1*) thomsonite, *2*) clinoptilolite, *3*) stilbite, *4*) heulandite[90].

Table 4. Oxidative dehydrogenation of methylcyclohexane on zeolites (450°, $CH_3C_6H_{11}:O_2 = 1:1.3$, volume velocity for methylcyclohexane $1\ h^{-1}$).[97]

Zeolite	Composition of product, %				W_{CO_2}, %
	C_6H_{12}	$CH_3C_6H_{11}$	$CH_3C_6H_8$	$CH_3C_6H_5$	
NaA	1.2	61.3	12.2	24.5	4.2
NaX	0.5	60.0	3.5	35.5	6.9
NaY	0.4	63.0	3.1	33.0	6.6
Na, K-chabazite	1.0	67.9	12.4	15.8	3.1
Na, K-erionite	0.3	77.4	13.6	8.4	2.8
0.25Fe-erionite	0.2	63.1	10.3	25.6	7.0
0.35Cu-erionite	1.3	60.5	11.2	26.2	5.1
Na, K-L	0.5	61.0	9.7	27.8	3.6
Na-mordenite	0.5	62.1	8.3	28.7	4.0

The influence of the structure and composition of the zeolite on the course of the reaction is even more marked in the oxidation of methylcyclohexane. The main product of the dehydrogenation of methylcyclohexane on metallic or oxide catalysts is toluene. There are published reports that only toluene is formed by the dehydrogenation of methylcyclohexane on 0.5% PtNaY zeolite[92], and that the partial dehydrogenation products which are formed in small quantities are converted into carbon. By studying the kinetics of the reaction and the carbonisation of the catalyst the authors concluded[92] that an intermediate dehydrogenation step is involved.

A recent patent[93] discloses that the reaction of methylcyclohexane on PtCaY zeolite at 505° yields toluent (55.2%), benzene (12.3%), and xylenes (17.0%). The bifunctional PtCaY catalyst apparently catalyses the dehydrogenation (on the platinum) of methylcyclohexane to toluene, which then undergoes disproportionation of the methyl group (on the acidic centres) to give benzene and xylenes. The dehydrogenation of alkylcyclanes to the corresponding aromatic hydrocarbons in the presence of Pt-zeolite catalysts has also been reported[94].

The oxidative dehydrogenation of methylcyclohexane on zeolite catalysts is discussed in detail in Refs.91 and 95–97, and it is shown that the direction of the reaction, the yields of the various products, and the selectivities of the process are a function of the composition and structure of the zeolite. Thus, on Na-faujasite the main reactions of methylcyclohexane are deep oxidation and oxidative dehydrogenation with formation of toluene[95]. The alkali cationic forms of chabazite and erionite are more active and selective towards the formation of methylcyclohexenes[97], but the type A and L zeolites (and mordenite) have a lower selectivity towards methylcyclohexenes than chabazite and erionite, though they yield methylcyclohexenes as well as toluene (Table 4). The low selectivity of the faujasites with respect to methylcyclohexenes can be explained, as in the cyclohexane reaction, by the strong adsorption of methylcyclohexane on these zeolites, which favours the more disruptive transformations within the internal cavities on the zeolite. On the other hand, on the narrow-pore zeolites the reaction takes place on the outer crystal surfaces, and the resulting cyclo-olefin intermediates can be desorbed into the gas phase and escape further dehydrogenation to toluene.

Table 5. Conversion of methylcyclohexane on cationic forms of type Y zeolite (450°, volume velocity 1 h^{-1}).[96]

Zeolite	Carrier gas	Conversion, %	Composition of product, %					W_{CO_2}, %
			C_6H_6	$CH_3C_6H_5$	$C_6H_5C_2H_5$	$(CH_3)_2C_6H_4$	$(CH_3)_3C_6H_3$	
0.48 HY	air	85.4	3.2	38.7	—	22.3	—	4.0
0.48 HY	helium	64.4	—	16.1	—	9.1	—	—
0.86 CaY	air	96.2	2.0	43.2	0.9	35.6	3.5	3.7
0.86 CaY	helium	48.0	1.3	8.7	0.2	8.3	1.6	—
0.60 MgY	air	85.9	1.5	31.5	—	9.2	—	3.6
0.60 MgY	helium	48.4	—	8.5	—	1.4	—	—
0.93 NdY	air	95.5	2.9	45.9	0.9	34.8	—	3.3
0.93 NdY	helium	90.8	1.3	38.5	1.0	28.4	—	—
0.60 NiY*	air	64.5	2.0	12.9	0.9	20.9	4.1	3.8
0.60 NiY*	helium	58.8	1.1	22.0	0.5	17.2	2.3	—
0.50 CoY	air	31.1	1.4	8.2	—	—	—	4.9
0.50 CoY	helium	10.3	—	2.5	—	—	—	—

*At 350 °C.

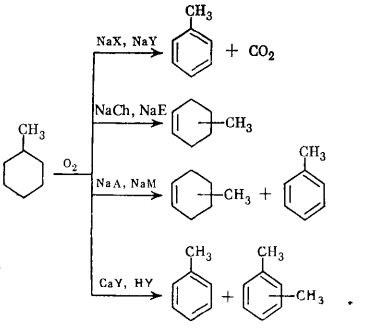
We note from Table 4 that the insertion of copper and iron cations into erionite increases the yields of toluene and carbon dioxide and thus lowers the selectivity of the reaction towards methylcyclohexenes[95]: in other words, zeolites containing transition metal cations tend to favour the more radical transformations of methylcyclohexane.

It has been shown[91,96] that in the presence of oxygen methylcyclohexane (unlike cyclohexane) reacts on decationated and on alkaline-earth cationic forms of type Y zeolite to give various aromatic hydrocarbons including toluene and xylenes (Table 5). In other words, the Ca, Mg, and NH_4 forms of type Y zeolite behave as typical bifunctional catalysts towards the oxidative transformation of methylcyclohexane into xylenes, even though their composition does not include Group VIII metals or transition-metal oxides. We may assume that the xylenes are formed by the oxidative dehydrogenation of methylcyclohexane to toluene, followed by disproportionation into benzene and xylenes. However, it appears from the distribution of products that benzene is always present in smaller amounts than the xylenes. Furthermore, under otherwise identical conditions the yield of xylenes from the disproportionation of toluene is smaller than from the reaction of methylcyclohexane, and therefore an alternative mechanism for the formation of xylenes from methylcyclohexane (by-passing the toluene formation step) cannot be excluded.

In a study[96] of the effect of the degree of decationation of type Y zeolite on the reaction of methylcyclohexane it was found that the yield of xylenes becomes progressively less sensitive to the presence of oxygen in the reaction mixture as the degree of decationation of the zeolite is increased. It has also been reported[98] that on decationated zeolite Y containing 3% Rh methylcyclohexane at 300° and 30 atm pressure undergoes isomerisation and hydrogenolysis reactions, giving various five-membered cyclic and aliphatic hydrocarbons.

The lack of activity of the alkali cationic forms of various zeolites and of amorphous alumina–silicas and aluminium oxide towards the oxidative conversion of methylcyclohexane into xylenes suggests that both acidic properties and a specific crystal structure are required to give an active catalyst[96]. Thus, decationated mordenite has a negligibly small activity for this reaction, and CaX zeolite gives a much smaller yield of xylenes than CaY.

The following reaction scheme reflects the main directions of the oxidative dehydrogenation of methylcyclohexane on zeolite catalysts (NaCh, NaE, and NaM are Na-chabazite, Na-erionite, and Na-mordenite respectively):



By varying the structure and composition of the zeolites over a wide range we can control the direction of the transformation of methylcyclohexane, and thus obtain desirable end-products. This flexible and selective application suggests that crystalline alumina–silicas will be used increasingly as practical oxidation catalysts.

IV. OXIDATIVE DEHYDROGENATION OF ALKYLAROMATIC HYDROCARBONS

The oxidative dehydrogenation of ethylbenzene on type Y zeolite containing transition metals was first reported by Venuto and Landies[5]. On MnY zeolite the yield of styrene was not higher than 8.7%. This low activity did not justify a detailed study of the oxidative dehydrogenation of alkylaromatic hydrocarbons on other types of zeolite.

However, more recent work[85,87,99-111] has revealed a number of interesting aspects of this reaction in the presence of zeolite catalysts. Thus, unlike the MnY zeolite, alkali cationic forms of various zeolites (free from transition metals) are catalytically active in the oxidative dehydrogenation of ethylbenzene and isopropylbenzene[87,95,100], the activity and selectivity of the catalysts and the specific features of the process being strongly influenced by the zeolite structure. Faujasites were found[100,104] to be more active towards deep oxidation, and therefore their selectivity towards oxidation dehydrogenation is low. Narrow-pore type A zeolites, chabazite, erionite, and mordenite are less active towards the deep oxidation and hence they offer a higher selectivity for the formation of styrene. Furthermore the yield of styrene on faujasites increases with time, a stable regime being established 2.5–3 h after the beginning of the reaction, whereas in the presence of narrow-pore zeolites this development period is not observed.

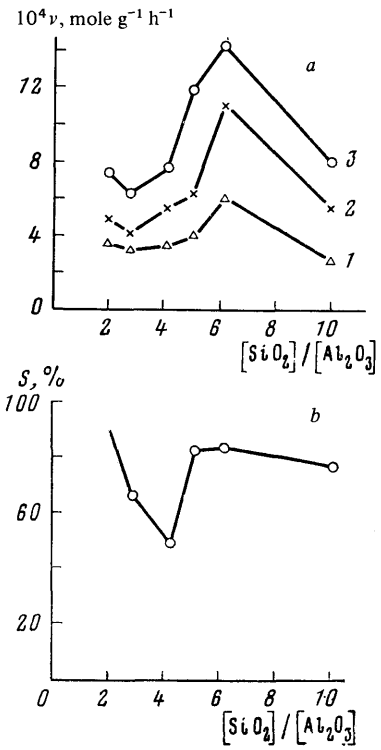


Figure 4. Rate of oxidative dehydrogenation of ethylbenzene (*a*) and selectivity with respect to styrene (*b*) against the $[SiO_2]/[Al_2O_3]$ ratio in zeolite at: *1*) 400, *2*) 425, and *3*) 450 °C (Ref.100).

The effect of the zeolite structure on the activity was investigated on the Na or Na, K forms of various synthetic zeolites[100]. The rates of oxidative dehydrogenation of ethylbenzene and the selectivities with respect to styrene are shown in Fig.4 as a function of the silica to alumina ratio in the zeolite[100]. In oxidation reactions with an O_2:ethylbenzene ratio of 0.4 the narrow-pore zeolites of the erionite type offer a higher activity and selectivity than the faujasites. It is interesting to note that on type A zeolites, chabazite, erionite, and mordenite, whose pores are too small to allow the ethylbenzene molecules to penetrate into the zeolite holes, the oxidative dehydrogenation takes place with a greater selectivity than on the wide-pore faujasites (Fig.4*b*).

Interesting results were obtained also in a study of the oxidative dehydrogenation of alkylaromatic hydrocarbons on synthetic sodalite[87], characterised by the smallest entry windows of any type of zeolite (2.6 Å), a high thermal stability, and a close-packed crystal lattice[17]. In the presence of Na-sodalite the reaction is detectable even at 350°, and at 525° the yield of styrene reaches 45%, making sodalite more active than any other synthetic zeolite towards the oxidative dehydrogenation of ethylbenzene.

The kinetics of the oxidative dehydrogenation of ethylbenzene on the Na, K form of erionite have been studied[102], and the reaction at 400–475° was found to be first-order in ethylbenzene. At temperatures below 425° a zero reaction order with respect to oxygen is observed, and at higher temperatures the dependence is of the Langmuir type. The rate-limiting step of the reaction is thought to be the interaction between weakly adsorbed ethylbenzene and oxygen on the outer surface of the zeolite crystals. The apparent activation energy is 31.5 kcal $mole^{-1}$.

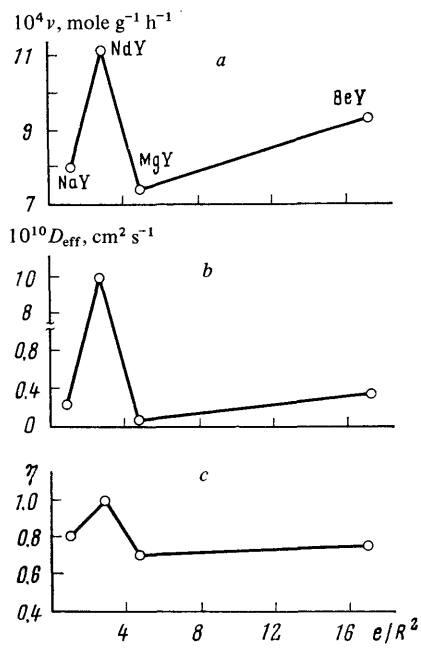


Figure 5. Rate of oxidative dehydrogenation of ethylbenzene (*a*), effective diffusion coefficient (*b*), and effectiveness factor (*c*) against the electrostatic potential of the cation in type Y zeolite at 425 °C (Ref.106).

The interaction of ethylbenzene with various zeolites has been studied by thermo-desorption[106]. Adsorption of ethylbenzene occurs only on type X and Y zeolites; only one desorption peak is observed, whatever the nature and concentration of the cation, and this peak is shifted towards lower temperatures when the sodium is exchanged for multivalent cations. Evidently, the strong adsorption of ethylbenzene on Na-faujasites is responsible for the deep oxidation

observed on these catalysts, and hence for the low selectivity with respect to styrene. From the thermo-desorption results we calculated[106] the activation energies for diffusion, the pre-exponential factors, and the effective diffusion coefficients of ethylbenzene in the zeolites. Plots of the rate of oxidative dehydrogenation of ethylbenzene, of the effective diffusion coefficient, and of the effectiveness factor against the electrostatic potential (e/R^2) of the cation in the zeolite are shown in Fig.5. We note that all three plots go through a maximum for the NdY zeolite, in which the reaction rate is least affected by diffusional limitations.

We have also studied[103,109] the catalytic properties of various types of natural zeolite towards the oxidative dehydrogenation of ethylbenzene and isopropylbenzene. The most active catalysts are heulandite and clinoptilolite, on which the yield of styrene varies between 37.7 and 48.2%. The apparent activation energy of the reaction for these natural zeolites is in the range 5–17 kcal mole^{-1}, i.e. it is lower than the apparent activation energy for synthetic zeolites of the chabazite, erionite, and mordenite types[100]. In the oxidative dehydrogenation of isopropylbenzene the catalysts form the same activity sequence as in the ethylbenzene reaction: the most active is clinoptilolite, and the least active lomontite. However, on all the zeolites the conversion of isopropylbenzene into α-methylstyrene is smaller than the conversion of ethylbenzene into styrene.

The catalytic properties of Pd-containing type Y zeolites towards the oxidative dehydrogenation of alkylaromatic hydrocarbons are discussed in Refs.101 and 107. It is shown that, unlike the starting NaY zeolite (which has a significant and stable activity towards the deep oxidation reaction), samples containing Pd(II) ions yield an amount of CO_2 which decreases as the time of operation of the catalyst increases, so that when steady state is reached the activity and selectivity of PdNaY towards styrene are relatively high. The activity and selectivity of this catalyst towards the oxidative dehydrogenation of ethylbenzene and isopropylbenzene are also higher than those of a Pd catalyst on amorphous alumina–silica.

The effect of the structure and composition of the zeolite on the activity of Pd-containing catalysts is discussed in Ref.110. Alkaline-earth and decationated forms of type Y zeolite have an initially high activity towards the cracking of ethylbenzene, but the yield of cracking products decreases with time, and after a development period small amounts of styrene can be detected. On an amorphous alumina–silica catalyst the yield of styrene decreases during the reaction. The introduction of palladium into CaY and HY zeolites and into amorphous alumina–silica lowers their cracking activity and increases the yield of deep oxidation and oxidative dehydrogenation products. However, all three samples are inferior to PdNaY zeolite in the yield of styrene and in the selectivity of the process. A possible explanation is electron deficiency of the palladium in CaY, HY, and amorphous alumina–silica as a result of the repulsion of the Pd 4*d* electrons by the acidic centres of the matrix. At the same time, because of the low acidity and of the weak electrostatic fields of the sodium cations, the influence of NaY on the valency state of the metal is much slighter[112]. We have shown[110] that the addition of Pd(II) cations to zeolites of the chabazite, erionite, and mordenite types increases their activity only in respect of deep oxidation, and as a result the Pd-containing zeolites of these types have a lower selectivity towards styrene formation than the initial zeolites.

The kinetics of the oxidative dehydrogenation of ethylbenzene on 0.5 wt.% PdNaY zeolite prepared by ion exchange have been investigated[111]. The reaction is kinetically of the first order with respect to ethylbenzene and of order 0.5 with respect to oxygen. The activation energy is 15 kcal mole^{-1}, i.e. about one-half of the activation energy of the same reaction on Na, K-erionite.[101]

By postulating the reaction scheme

$$O_2 + 2[\ ] \overset{k_1}{\rightleftarrows} 2[O]$$
$$C_2H_5C_6H_5 + [\ ] \overset{k_2}{\rightleftarrows} [C_2H_5C_6H_5]$$
$$[C_2H_5C_6H_5] + [O] \overset{k_3}{\rightleftarrows} [C_2H_3C_6H_5] + [H_2O]$$
$$[C_2H_3C_6H_5] \overset{k_4}{\rightleftarrows} C_2H_3C_6H_5 + [\ ]$$
$$[H_2O] \overset{k_5}{\rightleftarrows} H_2O + [\ ]$$

(where [ ] denotes an active centre on the catalyst surface, and [0], $[C_2H_5C_6H_5]$, $[C_2H_3C_6H_5]$, and $[H_2O]$ are adsorbed forms of oxygen, ethylbenzene, styrene, and water), and by taking as the slow step the desorption of styrene from the internal zeolite holes, we obtain the kinetic equation

$$v = v_{stat}(1 - e^{-k_4\tau})$$

where τ is time. This equation describes the changes in reaction rate in both the non-stationary and the stationary ($e^{-k_4\tau} \ll 1$) regime.

The oxidative dehydrogenation of ethylbenzene on the zeolite-containing catalysts AShNTs-3 and TsEOKAR-2 has been studied[113]. The yield of styrene at 525° on AShNTs-3 containing 20 wt.% of decationated zeolite Y was 31%; the selectivity of the process was 77%. The authors suggest[113] that the ethylbenzene molecule is adsorbed through the π-electrons of the benzene ring on a coordinationally unsaturated Al atom. On the "stronger" acidic centres the adsorption of ethylbenzene is stronger, and the molecule can undergo deep oxidation.

In the absence of oxygen isopropylbenzene can be dehydrogenated on zeolites[114,115] at high temperatures, but the selectivity is low and the reaction is accompanied by cracking of the initial hydrocarbon. Hence we may assume that the role of oxygen in oxidative dehydrogenation on zeolites is not to oxidise the hydrogen produced by the dehydrogenation of the hydrocarbon but to form carbon-containing intermediates which decompose to give styrene. This hypothesis is consistent with the low activity of zeolites containing no transition metals towards the dehydrogenation of hydrocarbons[114–117] and the oxidation of hydrogen[27,28].

V. OXIDATION OF INORGANIC COMPOUNDS

The reaction between hydrogen and oxygen is the simplest model reaction used to study the oxidation properties of catalysts. Ref.27 and 28 describe a study of the relative activities of type Y zeolites containing upwards of 50 equiv.% of transition-metal cations (Cu, Cr, Fe, Co, Mn, Ni, Ag). The highest activity was observed in AgY, followed by CuY, FeY, CrY, NiY, and CoY. The same activity sequence applies, on the whole, to the oxidation of CO, but in this reaction CoY is as active as AgY.

The activity of different cationic forms of type X zeolite towards the oxidation of hydrogen was found[118] to decrease in the series PdHX > CuHX > FeHX > NiHX > CrHX > ZnHX > MnHX > CoHX > HX. The activity of the CuHX sample increases with the concentration of copper ions in the zeolite. Copper cation pairs connected by bridging oxygen are suggested[118] as the active centres.

The main features of the oxidation of CO on zeolites containing transition metals are discussed in detail in Refs.119–127. The addition of up to 36% of copper is shown[119] to increase the activity in direct proportion, changing to an exponential dependence for copper contents

up to 90%. The reaction is first-order with respect to carbon monoxide and zero-order with respect to oxygen. The active centres are thought to contain more than one copper cation. The effect of the ion exchange conditions on the activity of the Cu(II), Cr(III), Ni(II), Co(III), and Fe(III) forms of type Y zeolite towards the oxidation of CO is discussed in Refs.120–122. Samples prepared at pH values corresponding to hydrolysis of the salts have a catalytic activity per atom 4–5 orders of magnitude greater than samples prepared under conditions in which the transition metals are stabilised as isolated ions. In the former case the metal cations are partly coordinated by an oxygen atom not belonging to the zeolite skeleton and having a high reactivity as a result of the greater covalence of its bond with the metal cation.

Isolated Cu(II) cations in zeolites have been shown[123] not to interact with CO at temperatures between −196 and 500°. Weak magnetic groups of associated Cu(II) cations form adsorption complexes with CO at temperatures between −196 and 100°, and at 300–500° they oxidise CO to CO_2 [the Cu(II) being reduced to Cu(I)]. Strong magnetic associations of Cu(II) cations, including bridging (non-skeleton) oxygen, can oxidise CO to CO_2 even at low temperatures.

A study of the oxidation of CO on X and Y zeolites containing cations with low charges has led to the conclusion[124] that CO molecules from the gas phase can react with dissociatively adsorbed oxygen in bridging positions. Very little oxygen is adsorbed on the Tl(I), Co(II), and Mn(II) forms, and none on the Cu(II) and Ni(II) forms, because of the difficulty of raising the oxidation state of these cations. The catalytic activity of all these samples is low. Zeolites containing Fe(II) and Cu(I) are more active, and they can chemisorb up to 0.5 oxygen atom per metal atom. The following reaction mechanism was proposed[124] from the kinetic results:

$$2\mathrm{Fe(II)} + {}^1/_2\mathrm{O_2} \rightarrow \mathrm{Fe(III)}{-}\mathrm{O^{2-}}{-}\mathrm{Fe(III)}$$
$$\mathrm{Fe(III)}{-}\mathrm{O^{2-}}{-}\mathrm{Fe(III)} + \mathrm{CO} \rightarrow 2\mathrm{Fe(II)} + \mathrm{CO_2}\,.$$

The series of decreasing activity for the oxidation of CO is given[125] as CoY > CuY > FeY > NaY > MnY. The activity of the initial NaY zeolite is quite high at 400° but falls off rapidly at lower temperatures. The authors conclude that the catalytic activity of these zeolites is determined by the presence of isolated metal cations on the surface. I.r. spectral studies have shown[126] that the interaction of CO and O_2 on the surface of zeolites containing transition-metal cations leads (at high temperatures) to the formation of physisorbed CO_2 and of surface carbonates, produced by the interaction of CO and O_2 with the cations.

A very steep, non-linear increase in the adsorption of CO on zeolite Y as a function of the degree of exchange of sodium by multivalent cations has been noted[127], and ascribed to the fact that the cations are located in S_1 sites where CO adsorption cannot take place.

Amorphisation of FeY and CoY by a shock wave[128] has little effect on the oxidation of CO. The activation energy changes by 1–2 kcal mole^{-1}, and the catalytic activity per atom remains almost the same. Obviously, the catalytic properties are determined mainly by the nature of the transition-metal ions in the zeolite and by the way in which these ions are bound to the surface.

A method of preparing a zeolite catalyst containing 10% of rare-earth elements and 0.3% of Pt for the re-oxidation of CO to CO_2 in the regeneration of cracking catalysts has been proposed[129]. The conversion of CO can be as high as 95.8%, and the catalyst is stable towards carbon, hydrogen, and olefins.

The oxidation of ammonia on Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Cr(III), and Ag(I) forms of type Y zeolite has been studied by a pulse method[27,28]. The reaction product on all the catalysts is molecular nitrogen, but on the Cr(III) and Ag(I) forms nitrous oxide is also found, the selectivity for this compound being ~25% on Ag(I)Y at 400°. A series–parallel reaction is postulated, in which the N_2O reacts with NH_3 to give N_2. The catalysts can be arranged in the following series of decreasing activity: CuY > CrY > AgY > CoY > FeY > NiY, MnY. We note that this activity sequence differs quite markedly from that of the corresponding oxide catalysts[130,131]: this may be due to differences in the type of chemical interaction during catalysis on zeolites and on oxides.

The oxidation of ammonia on Cu(II)Y zeolite at 160–185° was found to be kinetically of the first order in ammonia and of zero order in oxygen[132]. The activation energy is 36.7 ± 2.6 kcal mole^{-1} for samples with different extents of ion exchange. The presence of $[Cu(II)(NH_3)_4]^{2+}$ complexes in the large zeolite holes has been detected by ESR and i.r. spectroscopy. The authors suggest[132] rate limitation by the reduction of Cu(II) to Cu(I).

VI. OXIDATION OF OXYGEN- AND SULPHUR-CONTAINING COMPOUNDS

The conversion of methanol on zeolites in the presence of oxygen has been investigated[133–140]. On zeolites not containing transition metals the methanol was found to react only by an acid–base mechanism to give dehydration and etherification products[133,134]. In the presence of zeolites containing groups of associated cations the methanol is oxidised to CO, CO_2, and formaldehyde[134], and when the reaction is carried out on zeolites containing isolated transition metal cations the main product is ether.

On NaX zeolite containing 21.2% of Ag the conversion of methanol at 320–350° is 91%, with a selectivity of 87% towards formaldehyde[135]. In the presence of a large excess of oxygen the methanol is oxidised to CO_2 and H_2O almost quantitatively.

The effect of the preparative conditions on the activity of the Cu and Ag forms of types A and Y zeolites towards the oxidation of methanol is discussed in Ref.136. Conversion of the copper ions in the zeolite into an oxide ($\xrightarrow{H_2}$ Cu° $\xrightarrow{O_2}$ CuO) does not affect the yield of formaldehyde, but the overall extent of reaction increases because of an increase in the yield of CO and CO_2, which the authors ascribe[136] to the greater covalency of the Cu–O bond in CuO as compared to the Cu–O–Cu associated groups in zeolite. Reduction of the silver to the metallic state in zeolites increases the yield of formaldehyde very substantially, possibly by facilitating the electronic transitions attending the oxidative dehydrogenation of methanol.

Natural zeolites of the mordenite and clinoptilolite type have been used as methanol oxidation catalysts[137,138]. Decationation of mordenite lowers the yield of formaldehyde, while the yield of ether increases by a factor of 2. On the Cu form of mordenite the reaction sets in at a temperature 100 K lower than on the sodium or the decationated form[137]. Among the many cationic forms of clinoptilolite the highest activity and selectivity are found in the magnesium-containing decationated form[138].

On the Na, Ni, and Co forms of type X zeolite at temperatures below 300° the main product of the oxidation of methanol is dimethyl ether, but when the temperature is raised to 450° a large proportion of the ether is converted

into formaldehyde[139]. The specific catalytic activity of the samples goes through a maximum as the degree of exchange is increased, and decreases in the sequence NiX > CoX > NaX. The authors[139] point out that the activity of CoX samples with a low degree of exchange is not very different from that of the NaX zeolite. They suggest that the reaction involves either oxygen in the coordination sphere of the cation (non-skeleton oxygen) or oxygen resulting from the dissociative adsorption of O_2 from the gas phase on the zeolite.

CH_3OH, CH_4, and NO are oxidised on NaX zeolite after u.v. irradiation[140], with formation of surface carbonate, formate, and nitrate complexes. As in the case of some metal oxides, these photo-stimulated reactions on NaX zeolite seem to be associated with the presence of impurities or structural defects. According to Shchuklov and coworkers[141] the impurity centres consisting of a transition metal ion in zeolites can capture an electron and thus stabilise the chemically active positive holes formed by the u.v. irradiation. Stabilisation of the free radicals formed by the decomposition of organic peroxides can occur by an electron-donor or an electron-acceptor mechanism on the surface of NaX and NaY zeolites[142].

In an oxidising medium, isopropanol reacts on the polycationic Fe–Zn form of type A zeolite to give acetone[143]. The activity of the Fe–Zn form is much greater than that of the separate Fe and Zn forms of type A zeolite. The yield of acetone increases with the degree of exchange, but the order in which the Fe and Zn ions are introduced into the zeolite has little effect on the activity. It has been shown[144] that, unlike the Li and Na forms of type X zeolite (which catalyse only the dehydration of isopropanol), the K, Rb, and Cs forms are active towards the dehydrogenation of isopropanol to give acetone.

The oxidation of benzyl alcohol on various zeolites has been studied[145,146]. In the presence of decationated type Y zeolite benzaldehyde, benzoic acid, benzyl ether, and CO_2 are formed[145]. Hydrogen treatment of the catalyst at 500° lowers its activity towards the oxidation by 60%. The addition of pyridine to the reaction mixture lowers the overall conversion of the benzyl alcohol, whereas the addition of water increases the yield of benzyl ether and lowers the yields of the oxidation products. On the Cu(II)Y zeolite the main products are benzaldehyde, CO, and CO_2.[146] The kinetic order of the reaction is unity for both oxygen and alcohol. The active centres are thought to be Cu(II) cations located in large zeolite holes. A recent patent[148] describes the oxidation of benzyl alcohol to benzaldehyde on type X and Y zeolites containing transition metal cations. The addition of initiators (peroxides, halides, etc.) to the reaction mixture is shown to increase the yield of benzaldehyde.

The oxidation of hydrogen sulphide on zeolites was first reported[24] in 1961, but detailed studies of this reaction were published much more recently[149–152]. It has been shown by ESR that when H_2S is adsorbed on NaX zeolite at room temperature the addition of oxygen leads to the formation of chain radicals [$^{\cdot}S-(S)_x-S^{\cdot}$ and $HS-(S)_x-S^{\cdot}$] and ion radicals (O_2^-, SO_2^-, and SO_3^-), which take part in the oxidation reaction[149]. According to the authors the high catalytic activity of NaX zeolite is due to the very strong deformation of the H_2S molecule after adsorption, and to the ease with which an electron can be transferred with H–S bond breaking. Lin and Lunsford[150] studied the interaction of H_2S with oxygen on MgO, amorphous alumina–silica, NaY, and MnNaY. On the MgO surface S^-, S^{2-}, and sulphite ions are formed during the oxidation. On NaY zeolite hydrogen sulphide dissociates with formation of elemental sulphur; the addition of Mn(II) ions to the zeolite increases the formation of sulphur. On an amorphous alumina–silica surface the rate of oxidation of H_2S is negligibly small.

Chabazite tuffs of various compositions are very active towards the oxidation of hydrogen sulphide[151]. The high selectivity of the reaction for sulphur (>98%) in the presence of a large excess of oxygen (15-fold excess over stoichiometry) is specially noteworthy. The formation of SO_2 among the reaction products begins after a definite induction period, suggesting that this compound is formed by consecutive reactions. It has been shown[152] that the Mn(II)Y zeolite catalyses the oxidation of SO_2 at room temperature to the sulphate ion (strongly bound in the zeolite micro-pores). As the dehydration temperature of the catalyst is raised the Mn^{2+} cations migrate into less accessible sites, with a loss of activity.

In the oxidation of methyl mercaptan NaX zeolite is more active than NaY, and Na-mordenite is practically inactive[153]. The activity of the zeolite has been shown to be related to the density of the cations in the elementary cell. The optimum reaction temperature is 450°; at higher temperatures the degree of conversion increases, but the selectivity of the reaction becomes unacceptably low.

VII. CONCLUSIONS

It is clear from the results considered here that zeolite catalysts have a high activity towards the oxidation of various organic or inorganic compounds. The selectivity of the process, the course of the oxidative transformation, and the specific features of the reaction are determined by the structure of the zeolite, by the state of oxidation of the transition metals, and by the nature and concentration of the ion-exchange cations. Clarification of the activation mechanism of molecular oxygen and of the hydrocarbon on the zeolite surface as a function of the zeolite composition and structure should make a valuable contribution to our understanding of the mechanism of catalytic oxidation.

Oxidation on oxide catalysts may involve both the oxygen contained in the catalyst and oxygen adsorbed from the gas phase[154–157]. In the case of zeolite catalysts the oxygen in the skeleton is very strongly bound[158,159], and isotope exchange between the skeleton oxygen and oxygen from the gas phase in NaX and NaY zeolites cannot take place below 600°. The existence of strongly bound oxygen, adsorbed from the air during heat treatment of decationated type Y zeolite and retained after vacuum heat treatment at 550°, has also been reported[160–162]. The correlation between the number of molecules of chemisorbed oxygen and the amount of cation radicals formed suggests the involvement of oxygen in this process as a reactant[162]; the observation that oxidation properties are confined to dehydroxylated surfaces of decationated zeolites has led to the conclusion[163] that oxygen chemisorption occurs on anion and cation lattice vacancies.

Strong oxidation–reduction centres have been detected on zeolite surfaces in an ESR study of the adsorption of various organic compounds[164–166]. The adsorption interaction of naphthalene molecules with a Na-faujasite surface to give a donor–acceptor charge transfer complex suggests[167] that NaX and NaY zeolites can retain (after vacuum heat treatment) strongly bound oxygen which is responsible for the oxidation properties of these zeolite surfaces. The important contribution of chemisorbed oxygen to the oxidation properties of mordenite is stressed also in Refs.168–172.

The formation of oxygen anion radicals by adsorption on different cationic forms of faujasites has been reported[173-183]. In most cases the ESR signals from the oxygen anion radicals are observed after irradiating the sample with γ-rays, X-rays, or u.v. light. However, on the Li, Na, Ti, and Pd forms of type Y zeolite the oxygen anion radicals are formed by adsorption of oxygen on vacuum heat-treated samples[179-184]. A thermo-desorption study has shown[185] that oxygen is adsorbed in different amounts and in different states on the Mn, Co, Ni, and Cr forms of type Y zeolite. On CuY zeolite (an active oxidation catalyst, which adsorbs large amounts of oxygen) five different states of adsorbed oxygen, with different reactivities, have been detected[186]. Inactive O^{2-} oxygen, which does not take part in oxidation reaction, is also present on CuX zeolite[187].

The catalytically active oxidation centres in zeolites have been identified as associated groups of transition metal atoms coordinated by non-lattice oxygen[119-124]. The adsorption and catalytic properties of isolated ions in the zeolite are quite different from those of an ion pair bound by a bridging oxygen atom. Measurements by γ-resonance spectroscopy have shown the existence of this type (M–O–M) of cation pair[45,83]. The oxidation of simple molecules (CO, H_2) on these centres is assumed[156,188] to involve a collision mechanism,

$$M^{(n+1)+}—O—M^{(n+1)+} + H_2(CO) \rightarrow 2M^{n+} + H_2O(CO_2),$$

followed by oxidation of the transition metal ions (M^{n+}) by oxygen.

The oxidation of low-molecular-weight hydrocarbons on zeolites yields mainly deep oxidation products; zeolites containing transition metals are the most active towards this reaction. Therefore the reactivity of oxygen is often discussed in terms of this reaction. With naphthene and alkylaromatic hydrocarbons oxidative dehydrogenation takes place in parallel with the deep oxidation. However, whereas the zeolites containing transition metals are the most active towards the oxidation of low-molecular-weight hydrocarbons, Na faujasites show a high activity in the deep oxidation of cyclohexane, and in this case the introduction of transition-metal cations favours oxidative dehydrogenation with formation of benzene[62,73].

Unlike the faujasites, the Na forms of various narrow-pore zeolites catalyse the oxidative dehydrogenation of cyclohexane with formation of cyclohexene[84,88]; the Na forms of various zeolites are active also in the oxidative dehydrogenation of iso-pentylenes[60] and ethylbenzene[100]. However, whereas the faujasites have a lower selectivity than the narrow-pore zeolites for the formation of styrene, in the oxidative dehydrogenation of iso-pentylenes the selectivity of the Na faujasites is greater than that of narrow-pore zeolites in the Na form.

Thus, though the Na forms of faujasites have no weakly bound lattice oxygen[158] and adsorb very much less oxygen than zeolites containing transition metals[185,186], they can nevertheless catalyse the oxidative dehydrogenation of iso-pentylenes, cyclohexane, and ethylbenzene. This can be explained by postulating a difference in behaviour towards oxygen between a zeolite surface covered with an adsorbed hydrocarbon and a pure zeolite surface. Alternatively, the reaction can be assumed to involve the formation of carbon–oxygen intermediate complexes with oxygen from the gas phase: in this case the course of the reaction should be determined mainly by the interaction between the zeolite and the hydrocarbons.

Thermo-desorption studies have demonstrated the strong dependence of the adsorbate–absorbent interactions on the structure and composition of the zeolite, and on the nature of the hydrocarbon[61,89,106]. Thus, in the case of cyclohexane and ethylbenzene the low selectivity of the faujasites towards the oxidative dehydrogenation reaction stems from the strong adsorption of these hydrocarbons, which favours deep oxidation. The more selective, narrow-pore zeolites adsorb neither ethylbenzene[106] nor cyclohexane[89]. On the other hand, 2-methylbut-2-ene is adsorbed both on faujasites and on narrow-pore zeolites[61]. However, in this case the diffusion of the hydrocarbon in the narrow-pore zeolite is slower than in the faujasite, as shown by the relative values of the effective diffusion coefficient. This may also explain the greater activity of the narrow-pore zeolites towards the deep oxidation of 2-methylbut-2-ene, whereas the faujasites show more selectivity towards the formation of isoprene. Furthermore, as the ionic radius of the alkali metal cation increases, the rate of the deep oxidation of 2-methylbut-2-ene also increases, and the selectivity towards isoprene decreases, possibly as a result of the obstacles to the diffusion of the hydrocarbons in the zeolite Y pores resulting from the presence of large cations.

Thus, our survey of published data on the oxidation of various compounds on zeolites from the standpoint of the influence of the structure and state of the crystalline aluminosilicates on the course of the reaction has revealed some interesting features. The similarity in size between the zeolite pores and the oxidisable molecules gives rise to large changes in the selectivity of the reaction for a particular product from quite small changes in the ratio of these two sizes. The possibility of controlling the course of the transformation of a given hydrocarbon towards the formation of different products by varying the structure and the composition of the zeolite is very attractive. This combination of flexibility and selectivity suggests many potential applications of zeolite reactions in the oxidative transformation of hydrocarbons.

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