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Promotion of Aluminosilicate Catalysts by Reactants and Additives

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Experimental results are given on the promotion of aluminosilicates—amorphous and crystalline—by components of the reaction mixture (alkenes, halogen-containing compounds) and by molecules (water, nitrogen, carbon dioxide, etc.) not involved in the reaction stoichiometry. The effect of additives or reactant molecules on the catalyst depends on their structure and composition, as well as on the concentration of the promoter. A suggested mechanism of promotion of aluminosilicates and zeolites is considered. A list of 160 references is included.

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I. INTRODUCTION

Artificial and naturally occurring aluminosilicate catalysts and zeolites (constructed on an aluminosilicate frame) have found wide use in the petroleum-processing and petrochemical industry for the cracking of petroleum fractions, the alkylation of aromatic hydrocarbons, the polymerisation of alkenes, the isomerisation of alkylated aromatic hydrocarbons, *trans*-alkylation, and other processes[1-5]. The aluminosilicate catalysts are built of interconnected polyhedra such as $[AlO_4]$, $[AlO_5]$, and $[AlO_6]$ groups and the $[SiO_4]$ tetrahedron. They contain also hydroxy-groups and water molecules, either sorbed or structural. In zeolites aluminium is present in $[AlO_4]$ tetrahedra "stabilised" in the lattice by $[SiO_4]$ tetrahedra and by other groups. "Isolated" $[AlO_4]$ tetrahedra present in the structure of aluminosilicates and zeolites are the most active in catalysing the reactions of hydrocarbons, alcohols, and other compounds[6,7]. Zeolites are used also as matrices in the production of new zeolite-containing catalysts possessing excellent operating properties.

The efficiency of the industrial or laboratory conversion of various hydrocarbons and other compounds depends not only on the composition and structure of the catalyst but also on the composition of the initial mixture of reactants under otherwise similar experimental conditions, i.e. temperature, pressure, type of process, duration of continuous operation of the catalyst, and other variables. The activity of solid catalysts can be increased considerably (promoted) by the addition of reactant molecules or by introducing non-reactants into the reaction mixture. Such enhancement of the activity of a catalyst by oxygen molecules was first observed for liquid-phase hydrogenation[8]. In the Soviet Union work on the promotion of catalysts by reactant molecules was undertaken by Roginskii[9], who suggested that promotion of the solid surfaces was due to change in their structure and electronic state, departure of their compositions from stoichiometric, and the trapping of the promoting additives in surface defects on a metallic or oxide solid catalyst. More recently the idea has developed that promotion involves action on a solid surface by molecules of a promoter acting as a non-stoichiometric component in the catalysis[10]. This concept is phenomenological in character, like the ideas of variation in composition and properties of the catalyst under the influence of the reaction mixture[11] and like the deductions based on the formal kinetics of the interaction of a catalyst with reactant molecules[12].

The above paper[10] gave several examples of the activation of various catalysts by components of the reaction mixture or by molecules of substances specially added thereto. However, no systematic survey has been made of information on the change in activity and selectivity of aluminosilicates, varying in composition and structure, under the influence of reactant molecules or on the control of the activity and selectivity of catalysts by changes in the composition of the reaction mixture. It has now been shown that certain compounds present in a hydrocarbon reaction mixture promote the action of an aluminosilicate when they are present at certain concentrations, but deactivate the catalyst when present at other concentrations. Roginskii termed this phenomenon *modification*, and the additives themselves *modifiers*[9].

II. PROMOTION OF ALUMINOSILICATES BY ALKENES IN CRACKING, ALKYLATION, POLYMERISATION, AND HYDROGEN EXCHANGE

It was established as early as 1948 that alkenes act as promoters[13] in the isomerisation of hydrocarbons in the presence of halide catalysts. Later it was observed[14] that small (0.1—0.35 mole %) additions of octene to the reaction mixture on the cracking of n-octane enhance the activity of an aluminosilicate catalyst, with an increase in the conversion of the alkane approximately from 21% to 27%. Additions of more than 0.4 mole % of the alkene diminish the quantity of n-octane decomposed (Fig. 1): i.e. the catalyst is deactivated. The alkene itself may undergo partial conversion. However, it had undergone repeated preliminary involvement in the main process.

Experiments in which 0.27 mole % of radioactive ethylene $^{14}C_2H_4$ was added to the reaction mixture were made in order to obtain a more precise idea of the mechanism of the action of the alkene on the catalyst and on the conversion of n-octane. Radiometric analysis established[14] that at most 20% of the ethylene mixed with octane underwent transformation, and the molecular ratio of conversion of the former to that of the latter was ~1 : 100. This suggests that the effect of the alkene molecules is to change the energy state both of the catalytic centres and of the reactant molecules. The behaviour of alkene molecules mixed with alkanes and a catalyst probably differs from their behaviour in the purely thermal cracking of hydrocarbons, where unsaturated hydrocarbons inhibit breakdown of saturated hydrocarbons, which occurs by a radical—chain mechanism[15].

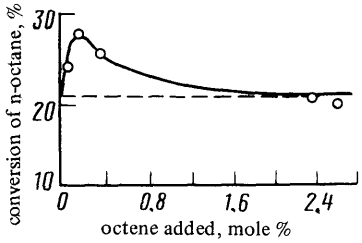


Figure 1. Effect of additions of unsaturated compounds on the cracking of n-octane at 518°C for 18 s. The broken line represents a blank experiment.

The promotion of an aluminosilicate catalyst by extremely small quantities (<0.01%) of alkenes was observed in the alkylation of aromatic hydrocarbons by alcohols[16-22]. Table 1 shows that, if a starting material isolated from the products of catalysis (which may contain alkenes) is subjected to alkylation, the yields are higher than those from the alkylation of the pure raw material (alkenes were detected by treating the catalysate with bromine water or potassium permanganate solution)[22].

Small additions of alkenes to the reaction system have a favourable effect on the hydrogen—deuterium exchange between isobutane and deuterium oxide in the presence of an aluminosilicate catalyst[23]: the rate of exchange in the presence of 0.5 vol.% of isobutene in the mixture was higher than in the absence of the alkene, although the activation energy of exchange was 17 kcal mole^{-1} in both cases. After alkenes had been removed from the mixture by hydrogenation, the rate of exchange decreased nearly to one-third[23] or exchange ceased completely[24] at high temperatures, in spite of the presence of alkenes.

Alkenes formed during the dehydrogenation of alkanes promote a catalyst containing platinum. Thus pure n-pentane does not undergo isomerisation in the presence of pure alumina under 7 atm at 220°C.[25] If a small quantity of platinum is deposited on the aluminium oxide, rapid isomerisation takes place. It was assumed[25] that platinum causes the formation of a small quantity of an alkene (or a carbonium ion), which is now able to isomerise on the acid carrier and again be hydrogenated to an alkane. We may suppose that the alkene itself is able to promote the platinum—alumina catalyst and enhance its isomerising activity.

Nevertheless, some alkenes tend to inhibit the conversion of others[26,27]. In the presence of an aluminosilicate catalyst containing nickel monoxide, for example, the polymerisation of ethylene is inhibited by 3—5% of propene or butene in the mixture. Yet the isomerisation of cyclopropane in the presence of an aluminosilicate or a cobalt oxide—aluminosilicate catalyst gives far higher yields in the presence of added ethylene or propene than in the absence of alkenes[28].

Table 1. Alkylation of benzene, toluene, phenol, bromobenzene, and chlorobenzene by propan-2-ol with a space velocity v = 0.2 cm^3 cm^{-3} h^{-1} at 250°C*.[22]

Molar C_6H_6 : R reactant ratio	Yield of alkylation products, mass%									
	cumene		cymenes		isopropylphenol		isopropylbromobenzene		isopropylbenzene	
	I	II	I	II	I	II	I	II	I	II
2:1	29.6	29.8	39.0	40.8	39.0	—	16.5	19.5	13.0	14.5
4:1	53.0	58.6	60.0	62.6	58.0	58.7	31.0	37.0	31.0	33.0
6:1	59.0	64.6	74.0	80.2	63.5	73.9	38.0	45.0	33.0	39.5
8:1	60.2	68.5	74.3	82.5	70.0	—	42.0	53.5	40.0	50.5
20:1	73.5	94.0	79.5	96.3	81.0	98.0	69.0	92.0	63.3	81.0

*(I) Fresh starting material; (II) starting material isolated from products of catalysis.

The above experimental results obviously indicate that small doses of alkenes added to a reaction mixture act as promoters of aluminosilicates. The optimum content of alkenes exerting an activating effect on catalytic centres is probably below 1%. Higher concentrations of alkenes usually tend to deactivate the catalyst, as shown by a decrease in the rate of the process.

III. PROMOTION OF ALUMINOSILICATES BY "INERT" CHEMICAL COMPOUNDS

It has been established experimentally that water, carbon dioxide, and other molecules added in certain quantities to the reaction mixture are able to promote aluminosilicates, zeolites, and γ-alumina in the reactions of hydrocarbons and other compounds or else to change their adsorptive capacity[29-51]. In turn, heating aluminosilicates and zeolites to a certain temperature enhances their activity towards deuterium—hydrogen exchange[41], polymerisation[7], cracking[29], etc.

The activity of an artificial aluminosilicate catalyst towards the cracking of cumene[29,30] varies with the quantity of water introduced into the system, passing through a maximum whose position depends on the composition of the catalyst, its method of preparation, and the drying conditions[52]. Thus Kaliko and Pervushina[30] first heated an aluminosilicate catalyst in a vacuum at 700°C for 700 h, then cooled it in the vacuum to 400°C, and passed cumene vapour through it. If the catalyst were absolutely dry, it exhibited no catalytic activity on contact with isopropylbenzene. The adsorption of 0.00035 mass % of water conferred considerable activity on the aluminosilicate, which increased with the sorption of additional quantities to reach a maximum at 0.2 mass % of water. Similar results were obtained when an aluminosilicate was treated with caesium hydroxide solution, ignited at 750°C, and then treated with water[30].

Table 2 shows that the catalytic activity of an aluminosilicate in the cracking of cumene passes through a maximum with variation in its water content[53]. This was attributed[54] to variation in the relative quantities of protic and aprotic centres. The promotion of aluminosilicates by water has been observed also [31,32,35] in cracking, isomerisation, deuterium—hydrogen exchange[24,51], and polymerisation[55].

Table 2. Effect of dehydration on the activity of an aluminosilicate catalyst in the cracking of cumene[53].

Time of treatment of catalyst at 700°C, h	Water remaining in catalyst, mass %	Relative activity
Initial	1.40	1
12	1.63	1
15	0.53	1.3
30	0.42	2.1
40	0.37	1.7
50	0.16	1.6

The reactions undergone by 2,2,3-trimethylpentane, 2-methylpentane, and n-heptane in the presence of an aluminosilicate catalyst, with and without addition of water to the reaction vessel, are mainly of the cracking and isomerisation type[48]. The activity of the catalyst passes through a maximum at different quantities of water vapour absorbed by the aluminosilicate in the two reactions: maximum cracking and isomerisation were observed with 2,2,3-trimethylpentane, 2-methylpentane, and n-heptane with water contents in the catalyst of respectively 0.1, 0.047, and 0.15 mass %. The results for the isomerisation of 2-methylpentane were identical with those of Ref. 26. With rise in temperature from 162 to 180 and then to 200°C the yields of products from n-heptane for the "dry" catalyst were respectively 7.53, 21.83, and 52.83 [%]; the corresponding yields for the "wet" catalyst (with the optimum water content of 0.1 mass %) were 44.30, 53.41, and 77.23 [%].

Table 3. Effect of water (supplied at 0.03 $cm^3\ cm^{-3}\ h^{-1}$) on yield of xylenes from the isomerisation of *m*-xylene fed at 0.3 $cm^3\ cm^{-3}\ h^{-1}$.[56]

Temp., °C	Yields, mass %			
	toluene	*m*-xylene	*p*-xylene	*o*-xylene
400	trace	67.8	14.7	9.3
450	2.5	51.1	16.7	18.5
470	9.7	47.2	12.5	17.5
450	3.7	55.0	13.6	13.6 (no water)

Aluminosilicates exhibited their maximum activity when they had adsorbed 0.05 mass % of water[31]. Yet the addition of water vapour[56] to ethylene diminishes its rate of polymerisation in the presence of an aluminosilicate catalyst containing nickel monoxide, and the yield of products of the isomerisation of *m*-xylene and its dismutation into toluene increases on the introduction of water into the reaction system (Table 3).

Nitrogen and carbon dioxide also promote aluminosilicates, as was observed in a study by a pulse method of the disproportionation of toluene[57] in currents of these gases in gas—liquid chromatographic apparatus. The kinetic results were processed quantitatively by the method of Refs. 58 and 59. The rate of disproportionation of toluene was higher in nitrogen than in hydrogen, as is shown by the equations—in a stream of hydrogen

$$K \cdot k = 34 \cdot 10 \exp(-30\,000/RT)$$

and in a stream of nitrogen

$$K \cdot k = 0.2 \cdot 10^{-1} \exp(-20\,000/RT)$$

where k (in s^{-1}) is the rate constant and K (atm^{-1}) the adsorption equilibrium constant. These indicate that conducting the disproportionation in hydrogen increases the activation energy, whereas in nitrogen fewer catalytically active centres function, but the process has a smaller activation energy. Thus hydrogen molecules slightly deactivate the aluminosilicate, whereas nitrogen molecules activate it. The pre-exponential factor is proportional to the number of active centres[60]. These results are supported also by data[61] on the polymerisation of hex-1-ene on aluminosilicate catalysts containing cobalt oxide. Thus the yield of liquid polymerisation products in the presence of hydrogen at 190°C is 7.6%, which rises to 22.6% when 7.0 vol.% of carbon monoxide is added. Crystalline aluminosilicates are promoted also by carbon dioxide[62,63].

IV. PROMOTION OF ALUMINOSILICATES BY GASEOUS HYDROGEN HALIDES

Artificial and native aluminosilicate catalysts were activated by pretreatment in a gaseous halogen or by a continuous supply of a hydrogen halide to the reaction zone. If a stream of gaseous hydrogen chloride is passed through a mixture of benzene, propene, and a catalyst, for example, alkylation can be effected with high yields at temperatures below the boiling point of benzene[64]. It is interesting that alkylation takes place more efficiently when the catalyst has first been completely dehydrated at temperatures above 500°C..

Gaseous hydrogen chloride also increases the yield when benzene is alkylated by alkyl halides at relatively low temperatures. This indicates that hydrogen chloride is a promoter of aluminosilicates in different reaction media, so that promotion is probably not due to formation of a protonated centre but to additional activation of the catalytic polyhedra.

In the absence of hydrogen chloride hardly any alkylation of benzene by ethylene occurs on aluminosilicate catalysts right up to 500°C.[65] Introduction of the gas into the stream of benzene and ethylene leads to an appreciable rate of alkylation to give a yield of 0.285 mole of ethylbenzene per mole of ethylene (at 450°C, with liquid benzene supplied at 0.075 mole $cm^{-3}\ h^{-1}$). Such alkylation is described[65] by the kinetic equation for a second-order irreversible heterogeneous reaction. The temperature dependence of the rate constant is

$$k = 2.77 \cdot 10^3 \exp(-90\,100/8.313T)\ . \qquad (1)$$

Increase in activity of an aluminosilicate on the addition of gaseous hydrogen chloride to the reaction mixture has been observed also in the isomerisation of n-butene[66] and in the alkylation of toluene by propene[67,68]. In these experiments the aluminosilicate had undergone preliminary treatment

with the gas for 1 h. The alkylation was conducted with molar proportions of toluene and propene of 2.3 : 1, a rate v = 1.1 $cm^3\ cm^{-3}\ h^{-1}$, and the catalyst functioning at 200°C for 1 h.

Table 4. Alkylation of toluene by propene[67,68].

Reaction products	Yields (× 100), mole $mole^{-1}$			
	aluminosilicate activated with HCl (gas)			Unactivated aluminosilicate
	initial	first regeneration	second regeneration	
Cymenes (total)	26.5	25.8	29.1	22.0
o-Cymene	23.5	25.0	23.4	25.8
m-Cymene	36.0	34.2	36.8	33.4
p-Cymene	40.5	40.7	39.8	40.8
Di-isopropyltoluenes	22.1	20.2	21.1	13.7
Hexenes	17.9	14.2	14.6	13.2

Table 4 shows that the high activity of an aluminosilicate treated with gaseous hydrogen chloride is preserved even after several cycles of regeneration in a current of air at 550°C for 3 h, but that the products of the alkylation of toluene by propene on activated aluminosilicates contain more *m*-xylene than is obtained with unactivated catalysts.

Other results[69,70] confirm the stable character of the centres produced in aluminosilicates by the action of gaseous hydrogen chloride. It was suggested[71] that the effect of the gas was to increase activity by forming more active centres than in the original aluminosilicate. Experimental data on the change in catalytic activity indicate that a gaseous hydrogen halide transforms $[AlO_n]$ polyhedra in the surface layer of the catalyst into polyhedra of mixed type $[AlO_nHal_m]$, with a change both in the composition of the polyhedron and in its acceptor power (n = 1—6 and m = 1—3). The $[AlO_4]$, $[AlO_5]$, $[AlO_6]$, and $[AlO_nH_m]$ polyhedra may undergo a change not only in symmetry and composition but also in energy state, which may influence the stability of intermediate complexes of reactant molecules with catalytic centres, and hence favour easier conversion of the reactant molecules.

V. PROMOTION OF ALUMINOSILICATES BY ALKYL HALIDES AND OTHER HALOGENATED COMPOUNDS

The alkylation of aromatic hydrocarbons by alkyl halides in the presence of aluminosilicates gives higher yields than do the pure alkenes[72-78]. This may be due to higher reactivity of the alkyl halides and to the promoting effect of these compounds themselves or of their decomposition products[79] on the catalytic centres of the aluminosilicates.

Carbon tetrachloride exerts a strong promoting effect on aluminosilicates in the alkylation of benzene by ethylene[80]: thus the temperature dependence of the rate constant in its absence is

$$k = 1.41 \cdot 10^{-6} \exp(-10\,000/RT) \qquad (2)$$

but on the addition of 0.3 mass % CCl_4 this becomes

$$k_1 = 2.63 \cdot 10^{-6} \exp(-10\,600/RT)\ . \qquad (3)$$

These results show an increase in rate of alkylation of some 80% in the presence of carbon tetrachloride. The higher pre-exponential term in the latter equation suggests that the intermediate complex of the catalytic centre with reactant and promoter molecules is "looser" than in the absence of tetrachloromethane, while the energy state of the complexes is almost the same in the two cases. Experimental results for the promotion of a catalyst by carbon tetrachloride are listed in Table 5. Termination of the supply of carbon tetrachloride to the reaction mixture results in a sharp decrease in the conversion of ethylene in the alkylation of benzene, whereas in the presence of 0.3 mass % CCl_4 raising the pressure and the molar ratio of benzene to ethylene increases the proportion of starting material converted.

Table 5. Effect of quantity of tetrachloromethane on conversion of ethylene on aluminosilicate catalyst under 20 atm at 250°C with molar velocity n_0 = 0.0357 mole $g^{-1}\ h^{-1}$*.[80]

Tetrachloromethane added to benzene, mass %	Conversion of ethylene, %
0.0	35
0.1	42
0.2	50
0.3	75
0.5	75

* Molar ratio of benzene to ethylene γ = 2.7 : 1.

It is interesting that aluminosilicates differing in composition are unequally activated by an alkyl halide (ethyl chloride) in the alkylation of benzene by ethylene. Fig. 2 shows that an aluminosilicate containing 30 mass % Al_2O_3 + 70 mass % SiO_2 is most strongly promoted by ethyl chloride or its decomposition products. These results will be explained[81-83] in Section VIII.

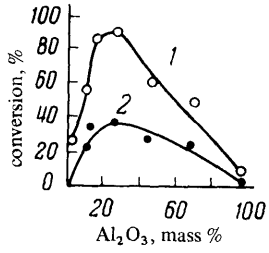


Figure 2. Activity of aluminosilicate catalysts, differing in composition, in the alkylation of benzene by ethylene with the addition of ethyl chloride (benzene supplied at n_0 = 0.0357 mole $g^{-1}\ h^{-1}$ under 3.0 atm): 1) 0.3 mass % C_2H_5Cl added to benzene; 2) pure $C_6H_6 + C_2H_4$ mixture.

The character and the magnitude of the effect of alkyl halides on aluminosilicate catalysts depend also on the composition and structure of the compound introduced into the reaction mixture. Table 6 shows that hydrocarbons in which geminal hydrogen atoms have been replaced by halogen atoms activate aluminosilicates more strongly than do their isomers with a different arrangement of

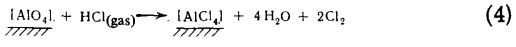
halogen atoms. The greater the number of geminal halogen atoms in a compound, the stronger usually is its promoting action on a catalyst. Compounds containing bromine or fluorine atoms have a weaker activating effect on an aluminosilicate than have compounds containing only chlorine atoms. Halogen-containing compounds of vicinal structure generally lower the activity of an aluminosilicate catalyst towards alkylation.

Table 6. Alkylation of benzene by ethylene in presence of an aluminosilicate catalyst (containing 16 mass % Al_2O_3) with $\gamma = 2.7:1$ and $v = 1.2$ cm^3 cm^{-3} h^{-1} at 300°C.[80]

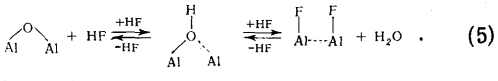
Halogenated compound	Quantity added to benzene, mmoles $(100\ g)^{-1}$	Ethylene converted, %	Ethylbenzene in products, %
CCl_4	1.95	93.5	96.5
$CHCl_3$	2.50	77.8	90.8
CH_2Cl_2	3.52	47.0	83.2
C_2H_5Cl	4.65	89.5	96.0
C_2H_5Br	2.75	68.9	89.0
CBr_4	0.90	61.4	88.2
1,1,1-$C_2H_3Cl_3$	2.25	71.4	96.5
1,1,2-$C_2H_3Cl_3$	2.25	31.2	64.1
1,1-$C_2H_4Cl_2$	3.03	55.2	97.5
n-C_3H_7Cl	3.81	52.5	94.8
i-C_3H_7Cl	3.81	58.4	95.2
1,2-$C_2H_4Cl_2$	3.03	18.1	66.2
1,2-$C_3H_6Cl_2$	2.66	25.2	—
$FCCl_3$	2.18	83.4	98.3

The data in Table 6 suggest that the promoting or deactivating effect of additives on a catalyst is due to undecomposed hydrogen halide molecules. However, decomposition products of halogenated compounds—alkenes and hydrogen halides—may play some part. The activity of an aluminosilicate catalyst towards the conversion of hydrocarbons passes through a maximum depending on the quantity of alkyl halide added to the reaction mixtures[67,68]. Thus in the alkylation of toluene by propene under 1 atm at 240°C the maximum growth in activity of the catalyst was obtained on addition of 1.4 vol.% of isopropyl chloride to the reaction mixture. Gaseous hydrogen chloride and propene were detected among the reaction products. This confirms that aluminium silicate can be promoted in a high-temperature reaction not only by the reactant molecules but also by gaseous hydrogen chloride and by an alkene. It is assumed also that hydrogen chloride molecules can be sorbed by catalytic centres of the aluminosilicate, thereby displacing products or impeding the sorption of compounds responsible for the formation of "carbon" and other highly condensed products. This preserves accessibility to catalytic centres for the initial reactant molecules and thereby maintains high catalytic activity in the aluminosilicate for a longer time. This suggestion has found confirmation[84,85].

It is also possible that polyhedra of novel chemical composition may be formed by interaction between gaseous hydrogen chloride molecules and the aluminium—oxygen polyhedra:



(4)



(5)

Scheme (4) confirms that aluminosilicate catalysts containing fluorine but no hydroxy-groups[86] are extremely active in the isomerisation and the polymerisation of hydrocarbons, despite the diminished acidity of the centres. The appearance of centres of the type AlO_nHal_m in an aluminosilicate under the influence of gaseous hydrogen chloride is indicated by data on the isomeric composition of products of the alkylation of toluene by propene in the presence of an aluminosilicate catalyst and aluminium chloride. Table 7 shows that increase in the isopropyl chloride content of the mixture in the presence of the catalyst is accompanied by an increase in the *m*-cymene content of the products, until the equilibrium concentration is reached. A similar pattern is observed with rise in temperature of the alkylation of toluene by propene in the presence of aluminium chloride. The increase in the *m*-cymene content of the mixture in the former case is probably due to an increase in the number of halogenated catalytic centres formed in the aluminosilicate by scheme (4), which affect the isomerisation of *o*- and *p*-cymenes into the *meta*-isomer. This is evident from the fact that the composition of the cymene fraction in the former case approaches the composition obtained in the presence of aluminium chloride.

Table 7. Isomeric composition of products of the alkylation of toluene by propene.

Catalyst	T, °C	Molar toluene/propene ratio	Isopropyl chloride added, vol.%	Cymene fraction, %			Ref.
				ortho	*meta*	*para*	
Aluminosilicate	240	3.32:1	—	20.2	38.9	40.9	67
		3.54:1	1.43	15.1	44.9	40.0	67
		4.74:1	6.0	10.0	52.5	37.5	67
		3.56:1	100*	10.0	52.4	37.6	67
Aluminium chloride	100	—	—	18.9	48.1	33.0	87
	80	—		25	43	25	87
	20	—	—	17	44.2	38.8	88

* Alkylation by pure isopropyl chloride.

The promoting action of halogenated compounds—not of their decomposition products—on the catalytic centres of aluminosilicates can be revealed by an investigation at relatively low temperatures, at which the molecules of the halogenated compounds remain unchanged.

VI. PROMOTION OF ALUMINOSILICATES IN LOW-TEMPERATURE REACTIONS

Examples of low-temperature reactions are the polymerisation of pentenes and the liquid-phase alkylation of benzene by propene. In the presence of aluminosilicate catalysts quite high rates of polymerisation are observed[89-93] even between −20 and +60°C, with 60—70% conversion. The activity of an artificial catalyst can be further enhanced by the action of carbon tetrachloride introduced into the reaction mixture. In Fig. 3 the relative conversion of a mixture of pentenes is plotted against the quantity of tetrachloromethane added to the mixture[79]. Every point was obtained from the dependence of the yield of reaction products on time of contact at 20°C. Fig. 3 shows that the addition of up to 0.5 vol.% of carbon tetrachloride to the reaction mixture increases the proportion of pentene converted by roughly 50%.

Dichloroethane and diethyl ether have a similar effect on aluminosilicates[79]. Addition of 0.2 mass % of the former or 0.1 mass % of the latter increases the yield of polymerisation products from a mixture of pentenes at room temperature by 100—200% in comparison with the pure pentenes. Fig. 4 shows that the activity of the catalyst depends on the quantity of dichloroethane or ether added to the reaction mixture, and may pass through a maximum. In the presence of dichloroethane the activity of a promoted catalyst is higher than that of an unpromoted catalyst at all the concentrations studied. With ether, however, increasing its quantity above an optimum value entails strong deactivation of the catalyst. This indicates that alkyl halides and ether have different effects on the aluminosilicate centres and on the reactants.

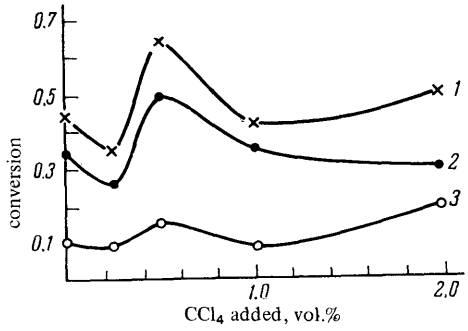


Figure 3. Effect of quantity of carbon tetrachloride added on the polymerisation of a mixture of isopentenes at 20°C for 120 min: 1) conversion of monomers; 2) yield of dimers; 3) yield of trimers.

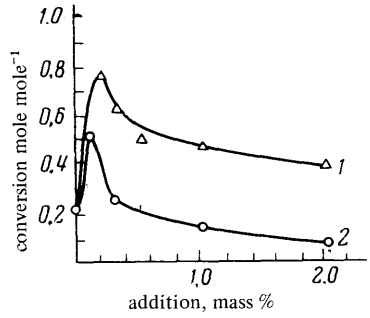


Figure 4. Dependence of conversion of a mixture of isopentenes at 20°C with time of contact 130 min on quantity of: 1) 1,2-dichloroethane; 2) diethyl ether.

Industrial aluminosilicate catalysts (including those containing zeolites) are contaminated by compounds of sodium, potassium, calcium, and other cations, which may have diverse effects on the catalytic activity[93,94]. Alkali-metal ions usually lower the activity of aluminosilicates towards the conversion of hydrocarbons. Halogenated compounds enhance considerably the activity of catalysts containing alkali-metal ions, probably in polyhedra of the type $[MO_4]$. This applies to reactions of hydrocarbons both at high and at low temperatures.

Aluminosilicates containing sodium and potassium ions are obtained by treatment with aqueous solutions of the chlorides[95]. Table 8 summarises results on the polymerisation of pentenes in the presence of such catalysts at 20°C, with and without the addition of carbon tetrachloride to the reaction mixture. It shows that aluminosilicates containing sodium and potassium ions exhibit less intense catalytic activity towards the polymerisation of pentenes than do those not containing such ions, and that potassium ions deactivate the catalyst more strongly than do sodium ions. The addition of 0.5 vol.% of tetrachloromethane to the reaction mixture almost completely restores the activity of a "poisoned" aluminosilicate, a potassium aluminosilicate being promoted more strongly than the sodium compound.

Table 8. Initial rates of polymerisation of a mixture of pentenes at 20°C.[95]

Soln. to treat catalyst	CCl_4 added, vol.%	Initial rate (× 10^4) of conversion, moles g^{-1} h^{-1}	Soln. to treat catalyst	CCl_4 added, vol.%	Initial rate (× 10^4) of conversion, moles g^{-1} h^{-1}
—	0	3.37	1.0*N* NaCl	—	1.33
—	0.25	2.57	0.3*N* NaCl	0.5	2.53
—	0.5	4.57	0.5*N* NaCl	0.5	2.96
—	1.0	3.24	1.0*N* NaCl	0.5	2.30
—	2.0	1.78	0.1*N* KCl	—	0.21
0.1*N* NaCl	—	2.44	0.1*N* KCl	0.5	3.21
0.5*N* NaCl	—	1.44			

An aluminosilicate treated with sodium chloride solution exhibits low catalytic activity also towards the alkylation of benzene by propene[96]. With a molar ratio of benzene to propene of 2.56 and v = 0.44 cm^3 cm^{-3} h^{-1} at 320°C the yield of isopropylbenzene is 38.7%, which falls to 3.7% on an aluminosilicate catalyst poisoned by sodium ions. The introduction of 3 mass % of propyl chloride into the reaction mixture with the "poisoned" aluminosilicate enables the yield to be raised again to 20.5%.

Thus halogenated compounds promote aluminosilicates both in high-temperature reactions of various hydrocarbons and in low-temperature reactions. The halogen compounds activate not only ordinary industrial aluminosilicate catalysts but also catalysts that have been "poisoned" by alkali-metal salts and other compounds.

VII. PROMOTION OF ZEOLITES

Original papers and reviews have been published on the structure of zeolites[97,98] and on their catalytic activity[99-103], showing that the latter depends on the nature, composition, and structure of the crystal lattice, as well as on the type of cations present in the polyhedra[104-106]. Alkali-metal ions usually deactivate a zeolite towards the reactions of hydrocarbons, and change the selectivity in isomerisation and in other reactions; but ions of bivalent and tervalent metals enhance the catalytic activity of zeolites. The activity of zeolites of various types can be changed (increased or decreased) by introducing into the hydrocarbon mixture halogen-containing compounds[71], carbon dioxide[115], certain organic acids, and other compounds of donor[96] or acceptor type.

Thus an NaY-type zeolite does not catalyse the transformation of hydrocarbons, in particular the isomerisation of *o*-xylene into *p*- and *m*-xylenes, at temperatures below 500°C.[107] Addition of gaseous hydrogen chloride up to a partial pressure of 0.05 gauge atm in the stream of hydrocarbons ensures 10% conversion of *o*-xylene, which can be increased to 15% by raising the partial pressure to 0.1 gauge atm. A zeolite of type MnY can be promoted for the alkylation of toluene by methanol when gaseous hydrogen chloride is supplied continuously into the flow of reactants (Fig. 5).[108]

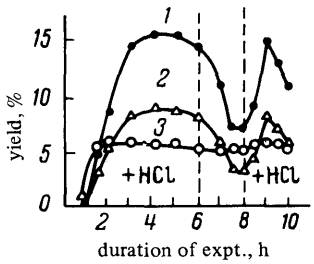


Figure 5. Effect of gaseous hydrogen chloride on activity of MnY-type zeolite in the alkylation of toluene by methanol (γ = 2:1) at 225°C as shown by yields (%) of: 1) *p*-xylene; 2) *m*-xylene; 3) *o*-xylene.

The activity of an NaX-type zeolite[109] is determined by the partial pressure of gaseous hydrogen chloride and depends on the degree of exchange of sodium for calcium or cerium(III) ions. When such ionic substitution reaches 30%, the zeolite is not activated by gaseous hydrogen chloride. The yield of cumene formed by alkylation is increased from 15% to 25% when 40% of the sodium ions in the zeolite have been replaced. Some of the hydrogen chloride molecules are strongly sorbed, while others are weakly sorbed. The rate of reaction is assumed to be proportional to the number of weakly sorbed molecules, which are responsible for promoting the zeolite.

The action of hydrogen bromide, water, and hydrogen chloride molecules on the catalytic centres in an REX-type zeolite (RE = rare-earth element) in the alkylation of benzene by ethylene can be traced from published data[110]. The zeolite was first ignited at 400°C and kept in a vacuum of 0.2 mmHg for 0.5 h, after which hydrogen bromide, water, or hydrogen chloride (1.85 mg-equiv.g^{-1}) was introduced into the system, and benzene was alkylated with ethylene at 177°C (C_6H_6 : C_2H_4 = 12 and v = 8.5 s^{-1}). Fig. 6 shows that, with short times (<50 min) of contact of the reaction mixture with the zeolite, the sequence of activating effects of the additives is HCl > H_2O > HBr; on prolonged (>100 min) operation of the zeolite this sequence changes to H_2O > HBr > HCl; and if the catalyst had operated for <25 min, added water and hydrogen bromide tended to deactivate the catalytic centres. It may be supposed that the catalytic centres on the fresh zeolite already possess the highest activity, so that the above three polar molecules are first sorbed on them. This leads to some diminution in acceptor power and hence in catalytic activity of the [AlO_4] tetrahedron. With increase in duration of operation of the zeolite its catalytic centres become covered with condensation products of high molecular weight or "carbon". Under these conditions the sorption of water, hydrogen bromide, or hydrogen chloride on them preserves[110,111] their enhanced catalytic activity in the transformation of hydrocarbons.

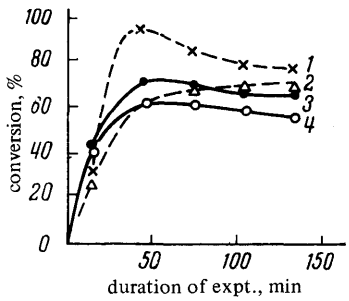


Figure 6. Variation of activity of REX-type zeolites with additions of: 1) H_2O; 2) HBr; 3) HCl; 4) pure zeolite.

Faujasite of NaY type is completely inactive in the cracking of cumene[112]. Quite high activity results from the introduction of gaseous hydrogen chloride, when the yield of cracked products is proportional to the surface coverage of the catalyst with the halide. It is assumed that a new catalytic centre is formed[113]:

$$M^+Z^- + HCl \rightleftarrows \begin{matrix} M^{+\delta'} & \ldots & Z^{-\delta''} \\ \vdots & & | \\ Cl^{-\delta_1} & & H^{+\delta_2} \end{matrix}$$

However, the increased chlorine content of the mixture[114] is insufficient to increase the activity of the zeolite significantly. The formation is probably necessary of centres with a definite structure and composition, i.e. a definite polyhedron, e.g. [AlO_nCl_m]. Polyhedra of this type have been detected by nuclear magnetic resonance when a zeolite is treated with chlorine at high temperatures[115].

The activity of zeolites, like that of aluminosilicates, can be enhanced by the action of alkyl halides and other compounds[96]. Table 9 shows that propyl chloride promotes zeolites of types NaX, NaY, CaX, and HX, but tends to deactivate CaY. The activity of a zeolite passes through a maximum, whose height and position depend on the type of zeolite, with increase in the quantity of propyl chloride added to the reaction mixture. The HX zeolite is almost twice as active as CaX towards the alkylation of benzene by pure propene. When propyl chloride is added to the reaction mixture, the yields of cumene on CaX approach those on an HX type. The NaY zeolite does not catalyse the alkylation of benzene by pure propene, but a markedly different picture is obtained when 3.0 mass % of propyl chloride is added to the system: the yield of cumene is then 0.173 mole per mole of the alkylating agent, which increases to 0.55 mole $mole^{-1}$ in the presence of 10 mass % of propyl chloride (calculated on the benzene). The alkylation of benzene by pure n-propyl chloride gives a yield of isopropylbenzene of only 0.104 mole $mole^{-1}$.

It is interesting that the activity of zeolites used in the alkylation of benzene by propene to which propyl chloride has been added remains fairly high after regeneration.

As mentioned above, this effect is connected with the appearance of new polyhedra in the zeolite under the influence of decomposition products of alkyl halides. The activity of the promoted zeolite diminishes after several regeneration cycles, but remains above that of the initial zeolite. This indicates that regeneration of a promoted zeolite by atmospheric oxygen and other molecules entails the breakdown of a number of chlorine-containing catalytic centres.

Table 9. Alkylation of benzene by propene with additions of propyl chloride and propan-2-ol under atmospheric pressure at 320°C.[96]

Alkylating agent and promoter, mass % on benzene	Rate of supply of benzene, $cm^3\ cm^{-3}\ h^{-1}$	Molar C_6H_6/C_3H_6 ratio	Yield (× 100) based on alkylating agent, mole $mole^{-1}$		
			cumene	di-isopropylbenzenes	
				meta	*ortho*
HX zeolite					
C_3H_6	0.46	2.50	19.1	2.5	1.5
C_3H_6 + 3% n-C_3H_7Cl	0.46	2.75	31.6	3.4	2.2
C_3H_6 + 10% n-C_3H_7Cl	0.45	2.52	33.2	1.8	1.1
C_3H_6 + 20% n-C_3H_7Cl	0.42	2.90	37.4	1.4	1.0
n-C_3H_7Cl	0.44	3.00	29.7	1.1	0.7
C_3H_6 + 3% i-C_3H_7OH	0.44	2.90	18.0	2.8	2.4
CaX zeolite					
C_3H_6	0.53	3.12	12.1	1.2	0.8
C_3H_6 + 0.5% n-C_3H_7Cl	0.57	3.10	21.3	2.2	1.2
C_3H_6 + 10% n-C_3H_7Cl	0.53	2.30	34.5	1.4	0.9
C_3H_7Cl	0.52	3.00	17.8	0.4	0.3
NaY zeolite					
C_3H_6	0.48	3.13	0.54		
C_3H_6 + 3% n-C_3H_7Cl	0.48	3.15	17.5	1.5	1.0
C_3H_6 + 10% n-C_3H_7Cl	0.43	2.07	55.0	2.7	1.5
n-C_3H_7Cl	0.47	3.00	10.4	—	—
Zeolite regenerated from previous expts. (C_3H_6 + 10% n-C_3H_7Cl)	0.47	2.80	32.7	4.0	2.3
Zeolite regenerated from previous expts. (C_3H_6)	0.48	2.82	23.3	8.3	1.7
CaY zeolite					
C_3H_6	0.52	3.7	50.0	3.4	1.8
C_3H_6	0.42	3.5	43.4	2.3	1.7
C_3H_6	0.42	3.0	46.5	2.2	1.1
C_3H_6 + 3% n-C_3H_7Cl	0.43	3.2	39.0	1.5	1.0
C_3H_6 + 9% n-C_3H_7Cl	0.41	2.4	26.7	1.2	0.6
C_3H_6 + 10% n-C_3H_7Cl	0.40	3.0	23.5	1.3	0.6

The activity of an NaY-type zeolite towards the alkylation of benzene by propene[98,116] depends on the molecular structure and type of additive. Table 10 shows that molecular chlorine, tetrachloromethane, n-propyl chloride, propionaldehyde, and acetone activate the zeolite. They can be arranged in the sequence

$$Cl_2 > CCl_4 > n\text{-}C_3H_7Cl \gg (CH_3)_2CO > C_3H_7CHO,$$

according to their activating effect on the zeolite. Propionic acid, nitropropane, and chlorobenzene have no activating effect on an NaY-type zeolite.

The presence of up to 3 mass % of water almost doubles the activity of zeolites also towards the cracking of isopropylbenzene[117-119], but the introduction of large quantities of water either has no effect or diminishes the activity. The activation of zeolites by carbon dioxide and by water is explained by surface protonation or by the formation of hydroxy-groups attached to silicon in the lattice, which are assumed to act as catalytic centres[118,119]. The promotion of zeolites by water has been observed also in the isomerisation of cyclopropane, the dehydration of alcohols[119,120], the disproportionation of toluene[121], the isomerisation of butenes[122] and xylenes[113], the alkylation of toluene by alcohol[123], and the polymerisation of ethylene and propene[124]. In many cases the change in catalytic activity of the zeolites when heat-treated at various temperatures depended on the quantity of residual water in the zeolite[110,111,120,123,125,126]. Promotion was explained by the action of molecules on "acidic" centres in the zeolite, although the structure of these centres and their energy state were not discussed.

Table 10. Alkylation of benzene by propene on NaY-type zeolite with various additives[116].

Alkylating agent and additive	Rate of supply of liquid benzene, $cm^3\ cm^{-3}[h^{-1}]$	Molar ratio, benzene : alkylating agent	Yield (× 100) based on alkylating agent, moles $mole^{-1}$		
			cumene	di-isopropylbenzenes	
				meta	*ortho*
C_3H_6	0.42	2.55	0.36	—	—
C_3H_6+3% n-C_3H_7Cl	0.485	3.15	17.3	1.5	1.0
C_3H_6+10% n-C_3H_7Cl	0.435	2.07	55.0	2.7	1.5
n-C_3H_7Cl	0.47	3.00	10.4	0.3	—
C_3H_6 (5th regeneration)	0.47	2.8	32.7	4.0	2.3
C_3H_6 (6th regeneration)	0.47	2.82	25.3	3.2	1.7
C_3H_6	0.468	3.03	0.96		
C_3H_6+3% C_3H_7CHO	0.455	3.20	2.0		
C_3H_6+3% C_3H_7COOH	0.420	2.36	0.8		
C_3H_6+0.5 $C_3H_7NO_2$	0.487	2.72	0.8		
C_3H_6+3% CH_3COCH_3	0.45	3.14	2.9		
C_3H_6+3% CCl_4	0.45	3.11	32.5	0.96	0.5
C_3H_6 (1st regeneration)	0.443	3.56	2.3		
C_3H_6+3% C_6H_5Cl	0.435	3.44	1.9		
C_3H_6+Cl_2	0.480	3.46	34.6	2.6	1.4

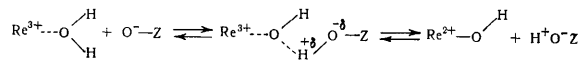
VIII. MECHANISM OF THE PROMOTION OF ALUMINOSILICATES AND ZEOLITES

Polymeric complexes, formed after adsorption of alkene molecules on catalytic centres, are assumed to play a definite part in the mechanism of the promotion[127-130] of aluminosilicate catalysts by alkenes. These hydrocarbons (propene, butenes) undergo rapid transformation with formation of a polymeric complex on an "acidic" centre of the aluminosilicate having degrees of polymerisation of 2–5.

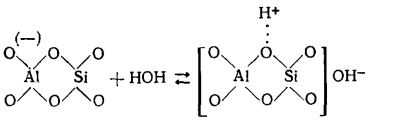
To establish the role of polymeric complexes in catalysis on aluminosilicates experiments were made on the isomerisation of but-1-ene[130] on an aluminosilicate containing polymeric perdeuteriobutene on the catalytic centre. On such a centre isomerisation yielded a large quantity of products in which the hydrogen atoms had been replaced in considerable number by deuterium. Yet hydrogen–deuterium exchange with an aluminosilicate surface that had undergone exhaustive deuteriation was comparatively small.

At low partial pressures of the alkene its degree of polymerisation in the complex is small and the activity of the catalyst also low. Both degree of polymerisation and catalytic activity increase with rise in partial pressure. Hence the effect of an alkene on an aluminosilicate catalyst depends on its degree of polymerisation with complex formation on an "acidic" centre. The optimum degree of polymerisation of ~3 units ensures the most active catalyst. The promotion of an aluminosilicate by an alkene may lead also to a change in the mechanism of isomerisation of alkenes, which is probably anionic at not very high temperatures.

The promoting effect of water molecules on aluminosilicate catalysts and zeolites is usually attributed to their ability to supply protons[131] to the surface. The transfer of protons is caused by the polarising effect of the cations, e.g. of a rare-earth metal, replacing ions in the zeolite:



A proton appears in the aluminosilicate catalyst by the mechanism



According to these schemes the catalytically active centre is a proton of a hydroxy-group attached to aluminium[131] or to silicon[35,66]. Nevertheless, direct experimental evidence has been published that the catalytically active centres in high-temperature and low-temperature reactions of hydrocarbons are aluminium—oxygen polyhedra[71,81,91,132-138], while the hydroxyl proton is able only to strengthen the accepting power of these polyhedra[137]. Furthermore, it is well known that silica has a high content of Si—O—H groups (even after ignition at temperature above 500°C), while their catalytic activity in the conversion of hydrocarbons is almost zero.

The promotion of zeolites by carbon dioxide is presumably[62,115] due to chemisorption of its molecules by sodium or calcium ions with activation of the catalytic centre. Chemisorption of carbon dioxide on a zeolite is regarded[115] as increasing the number of protons per unit surface, and hence enhancing the catalytic activity.

Kaliko and Pervushina[29,30] assume that water in aluminosilicates is present in both structural and adsorbed forms. Promotion is effected only by molecules adsorbed on catalytic centres. Catalysis of the conversion of hydrocarbons by aluminosilicates is supposed to involve active Lewis centres (aluminium three-coordinated with oxygen) or Brønsted centres[33]. However, such a view of the structure of the catalytic centre is incomplete and inconsistent with the geometrical limits of stability of the polyhedra. A coordinated triangle of type $[AlO_3]$ is unstable in aluminosilicates[139]. The ratio of the radii $r_{Al}/r_O = 0.418$ characterises the stability of $[AlO_4]$ and $[AlO_6]$ polyhedra. Triangular coordinated groups are stable only when this ratio is 0.15—0.22. The value 0.418 is the lower limit of stability of a coordinated octahedron. Hence only $[AlO_4]$ tetrahedra and $[AlO_6]$ octahedra are able to exist in aluminosilicates. The presence of such groups has been demonstrated in native aluminosilicates[97], artificial aluminosilicates, and zeolites[139,140].

Absorption of a water molecule is assumed to convert a Lewis centre into a Brønsted centre, a source of a proton which may be captured by hydrocarbon (e.g. alkene) molecules with formation of a carbonium ion, converted into the final products with regeneration of a proton. However, such an interpretation leads to difficulties in explaining the mechanism of the conversion of alkanes. Furthermore, it was shown experimentally that the activity of an aluminosilicate catalyst passes through a maximum with increase in the quantity of water introduced into the reaction zone, although most of the "aprotic" centres remain unoccupied by water molecules[141,142]. Danforth postulates[143] that water in an aluminosilicate acts as a cocatalyst, moving from centre to centre if the latter are contiguous. This results in displacement of the hydrocarbon from the complex catalyst and facilitates regeneration of the catalytic centre.

It must again be noted that heating aluminosilicate catalysts above 800°C leads to irreversible loss of their catalytic activity. The activity cannot be increased by addition of any quantity of water, so that the promotion of aluminosilicates involves catalytic centres having a different structure, which will be discussed below.

A convincing explanation of the promotion and deactivation of catalytic centres in aluminosilicates varying in type, structure, and composition was based on the view[71,81,91,132-138] that $[AlO_4]$ and $[AlO_6]$ polyhedra act as catalytic centres, with $[AlO_4]$ tetrahedra distributed as "islands" in a solid lattice, probably of defect (unsymmetrical] structure, catalytically the more active. Among artificial aluminosilicates the highest concentration of such tetrahedra is found in a catalyst containing 35—40 mass % of alumina and 65—60 mass % of silica[82]. Aluminosilicates of various compositions may contain "isolated", "island" $[AlO_4]$ tetrahedra, "condensed" $[AlO_4]$ tetrahedra, and "isolated" and "condensed" $[AlO_6]$ [octahedra].[82,83] The above aluminosilicate contains the maximum number of "isolated" $[AlO_4]$ tetrahedra. Artificial and natural aluminosilicates containing the largest number of such tetrahedra possess the greatest catalytic activity[134-138,144,145].

The degree of promotion of aluminosilicates by halogenated hydrocarbons depends on their alumina and silica contents[80]. Maximum promotion by ethyl chloride is observed[80] precisely with aluminosilicates containing 35—40 mass % of alumina, possessing maximum activity, and containing the maximum number of $[AlO_4]$ tetrahedra of "island" type. These results suggest that the promotion of aluminosilicates by halogenated and other compounds depends firstly on the content of $[AlO_4]$ tetrahedra of "isolated" type, secondly on the change in structure of the catalytic centre, and thirdly on the change in energy state of the catalytic centre and the reactant molecules.

The promotion of aluminosilicates by water, carbon dioxide, nitrogen, and other molecules may be attributed to a change in the acceptor properties of the $[AlO_4]$ tetrahedron or the $[AlO_nH_m]$ polyhedron in general, and to a change in the occupancy of unfilled $3d$ levels, possibly also in the symmetry of the tetrahedron. With small quantities of water, carbon dioxide, nitrogen, and other activating molecules sorbed on the catalyst surface the acceptor power of the catalytic aluminium—oxygen polyhedron may be increased by a change in the energy level of a vacant $3d$ orbital, which facilitates polarisation of a carbon—hydrogen bond in the hydrocarbon molecule, its cleavage, and reaction by a definite mechanism.

Andrianova and Roginskii considered[14] that the conversion of hydrocarbons on catalysts, whether promoted or not, had a radical—chain mechanism. Hansford[37] suggested a carbonium-ion mechanism, but this was not confirmed[142].

The promotion effect when halogen-containing compounds interact with catalytic centres in a zeolite or an aluminosilicate containing alkali-metal ions as $[MO_n]$ polyhedra (n = 4—6) can be attributed primarily to the action of the promoter molecule on the state of this polyhedron. Hence the increase in the activity of the catalyst under the influence of activating molecules may be due to the electronic (orbital) promotion of surface centres. The same phenomenon may occur under the influence of reactant molecules, with additional excitation of the catalytic centre. Interaction of activator with reactant molecules may further excite the latter. When activating

molecules of acceptor type interact with alkenes or with aromatic hydrocarbons, charge-transfer complexes are formed[146]. Such a complex has been observed with a mixture of chloroform and benzene[147,148].

Stepwise transfer of excitation energy along a layer of reactant and additive molecules sorbed on the catalyst surface may also occur. This is confirmed by the fact that a considerable proportion of benzene and carbon tetrachloride molecules (3% and 13% respectively) are already in excited vibrational states at room temperature[149]. This excitation may be transmitted to catalytic centres or reactant molecules and may promote these centres, changing their energy state and destroying the symmetry.

New catalytic centres resulting from chemical substitution may play some part in activating the catalyst[150]. Treatment of aluminosilicates or alumina with hydrogen halides produces Brønsted centres[151,152]. Partial replacement of hydroxy-groups by halogen atoms may also occur, with the formation of new active centres of Lewis[153] or Brønsted [154] type. However, treating aluminium oxide with fluorine compounds diminishes the acidity of the surface, while the catalytic activity towards the conversion of hydrocarbons increases sharply[155,156]. As mentioned above, the charge-transfer complexes themselves, e.g. that of an alkyl halide with an aromatic hydrocarbon, may have a considerable effect on the catalytic activity of the $[AlO_n]$ polyhedra. Transfer of charge may be effected from a 3*d* orbital of the halogen to a vacant π-orbital of the aromatic hydrocarbon or conversely; some compounds of this type are able to promote, whereas others deactivate, the catalytic centres.

Mixing benzene with molecules of considerable acceptor power, such as tetrachloromethane, hydrogen chloride, chloroform, and perchloroethane, yields associated charge-transfer complexes[157-159]. Associated complexes can be formed only with a certain acceptor concentration in the mixture, e.g. when the concentration of hydrogen chloride or chloroform does not exceed 0.02 mole per mole of benzene, above which concentration the resulting complexes already dissociate. The composition of the complex depends on the concentration of the solution. The stability of the complexes is connected not only with charge transfer but also with the stepwise migration of a proton. The latter is governed by the thermal motion and force fields of the benzene molecules.

Aromatic hydrocarbons mixed with ammonia, ether, dioxan, and other compounds of the same type form complexes in which the former act as acceptors and the latter as donors. Here the hydrocarbons have the role of aprotic acids, and the other reactants that of bases. These results can be related to the conversion, in the presence of aluminosilicates, of hydrocarbons mixed with acceptor or donor additives.

Certain acceptor additives to the reaction mixture may enhance the activity of aluminosilicates. Their activating effect, ability to form complexes with hydrocarbons, and promoting action are interrelated, as has been observed in the low-temperature[79,93,95] and high-temperature[68,116,104] reactions of hydrocarbons.

Donor molecules added in certain amounts to a reaction mixture usually lower the activity of aluminosilicates, although activation by donor molecules may be observed. Molecules of the reaction mixture may have a synergistic effect on the aluminosilicates in both cases: adsorption of a hydrocarbon on an aluminosilicate surface may lead to the formation of both radical-cations and radical-anions[160], the former by electron transfer from a molecular orbital of the donor molecule to a vacant atomic or molecular orbital of an aluminium—oxygen polyhedron, and the latter by electron transfer from a donor aluminium—oxygen polyhedron to a vacant molecular orbital of the hydrocarbon molecule. These centres may be adjacent, and it was assumed[160] that a donor catalytic centre contains an excess of oxygen atoms and favours conversion of an acceptor molecule into a radical-anion. With simultaneous or successive sorption of donor and acceptor molecules on the catalytic centres the catalytic activity of one centre may be strengthened by the other. Sorption of a donor molecule on an acceptor centre tends to strengthen the donor power of the donor centre. Conversely, sorption of an acceptor molecule on a donor centre will tend to strengthen the acceptor properties of the acceptor centre. This may be one reason why some concentrations of an additive will promote a catalyst, whereas other concentrations will deactivate it.

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