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REACTIONS OF OLEFINS IN THE PRESENCE OF METAL OXIDES

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CONTENTS

Introduction 445

I. Polymerisation of olefins 445
1. Non-conducting metal oxides 445
2. Semiconducting metal oxides 446

II. Isomerisation of olefins 448
1. Non-conducting metal oxides 448
2. Semiconducting metal oxides 449

III. Decomposition of olefins 450
A. Catalytic cracking 450
1. Non-conducting metal oxides 450
2. Semiconducting metal oxides 450
B. Low-temperature decomposition 450

IV. Redistribution of hydrogen 451
1. Non-conducting metal oxides 451
2. Semiconducting metal oxides 451

V. Hydrogenation of olefins, *ortho–para*-hydrogen conversion and deuterium–hydrogen exchange 451
A. Hydrogenation of olefins 451
B. *ortho–para*-Hydrogen conversion 452
C. Deuterium–hydrogen exchange 452
1. Non-conducting metal oxides 452
2. Semiconducting metal oxides 452

VI. Nature of the catalytic activity and the mechanism of the reactions of olefins in the presence of metal oxides 453
1. Non-conducting oxides 453
2. Semiconducting oxides 454

INTRODUCTION

Metal oxides are widely used as catalysts in organic chemistry. Of particular interest are the various reactions of olefins in the presence of oxide and aluminosilicate catalysts, especially the recently developed polymerisation over transition metal oxides to produce solid polymers. These oxides and those of Group II metals are usually semiconductors, while the oxides of Group III and IV metals and aluminosilicates are predominantly dielectrics.

This review deals with the literature and patent data on the chemical reactions of olefins (polymerisation, isomerisation, redistribution of hydrogen, cracking, hydrogenation, and deuterium exchange) in the presence of metal oxides. The catalysts fall into two groups, dielectrics and semiconductors, although in some cases this is an arbitrary distinction, since there is no sharp boundary between the two classes[1-4].

I. POLYMERISATION OF OLEFINS

1. Non-Conducting Metal Oxides

Aluminium oxide does not polymerise ethylene at pressures up to 70 atm and temperatures of 320°–380°,[5-10] propene at atmospheric pressure and 150°–200°,[11,12] isobutene at 600°,[13] normal C_{6-8} olefins at 350°, [14] or olefins of

pyrolysis gases at 500°–515°.[9] Ethylene polymerises at 260° and 300 mm pressure over Al_2O_3 activated at 460° in a vacuum[15]. There is slight polymerisation of normal butenes at 400°–450°, with simultaneous cracking and isomerisation[16,17], of pent-2-ene and 3-methylbut-1-ene at 400°, giving cyclic polymers[18], of hept-1-ene[19] and of certain C_{6-8} isoolefins[14] at the moment of their formation by the dehydration of alcohols. Marked activity is shown by Al_2O_3 activated with HCl,[20-22] HF,[23] $AlCl_3$,[24] or LiH.[25]

Silicon dioxide in the form of thermally activated silica gel[11,12,26,27] or obtained by the hydrolysis of ethyl orthosilicate[10,28,29] is inactive at temperatures up to 350°.[8,10-12,26-29] Over silica gel at 670°–700° olefins undergo partial decomposition, polymerisation, and aromatisation[30]. Literature references to the polymerising activity of silica gel[31-35] relate to technical samples containing oxides of Al, Fe, Ca, and Mg, *i.e.* essentially to aluminosilicates.

Aluminosilicates. *Floridin.* The polymerising activity of natural aluminosilicates towards olefins at room temperature was first shown by Gurvich[36-39], who used Floridin. Lebedev and coworkers showed[40-46] that Floridin activated at 275°–325° (with loss of 12–13% moisture) causes the polymerisation at room temperature of asymmetric di- and tri-substituted ethylenes, while ethylene and its mono- and symmetric di- and tetra-substituted derivatives do not react. However, propene and but-2-ene polymerise under pressure in sealed tubes[42,47] or at atmospheric pressure and 350° (to the extent of 6%),[28] and ethylene and other olefins from cracking gases polymerise at 340°–470° under pressure[6]. Floridin is activated by concentrated hydrochloric acid[28]. Isobutene polymerises between -80° and 200°,[43,45,46] and more vigorously the lower the temperature. Gaseous isobutene gave a complex mixture of dimer (~20%), trimer (~30%), and higher polymers; the liquid, sealed in a tube, gave after 3–24 days a mixture containing ~70% of higher polymers. Diisobutylene polymerises completely, and triisobutylene not at all. An isobutene polymer of average molecular weight up to 8000 was obtained at -65° over Floridin of low activity[43,48,49].

Clays. Isobutene is the most readily polymerised, butene and propene with more difficulty, and ethylene not at all[50]. C_{3-4} olefins are polymerised at atmospheric pressure[51-54] and under a pressure of 35–50 atm[55] at 50°–190°, producing dimers, trimers, and higher polymers. Clays are activated by air at 320°–500°; a yield of liquid polymerisate of ~80% has been obtained from isobutene[26,55-57]. Isobutene copolymerises with propene at 200°–300° and 10–25 atm over the Georgian clay gumbrine[58]. Isooctene is best polymerised at room temperature over clays of low silica content[59]. The dehydration of 2-ethylhexan-1-ol over gumbrine at 140°–164° is accompanied by polymerisation[60].

Kieselguhr. Kieselguhr from Kisatibi[61] is a highly active catalyst which does not require preliminary activation, and converts isobutene mainly to dimers; at 160° the yield of liquid polymers reaches 77%.

Over *bauxite*[31,57,62-64] activated at 665°–775° isobutene is 82–90% polymerised, but-1-ene 13–16%, and but-2-ene not at all.

Synthetic aluminosilicates. Silica gel containing 1% of alumina is an active catalyst for the polymerisation of propene[28] and isobutene[65-69]. Water vapour, traces of alkali, ammonia, oxygen, and sulphur compounds deactivate the catalyst. Iron and magnesium silicates are inactive in polymerisation reactions. The isobutene polymerisates obtained over synthetic aluminosilicate, Floridin, and "solid" phosphoric acid were very similar in composition.

The most active synthetic aluminosilicate catalyst contains 10–12.8% Al_2O_3.[11,12,29,70-74] At the optimum temperature of 160° isobutene gave a liquid product which was 97% di- and tri-isobutylenes[70]. n-Butenes and n-pentenes polymerise at 400°–450°.[75] The maximum yield of isobutene–propene copolymers (heptenes) is obtained at 250° and 25 atm,[58] and of isobutene–2-methylbut-2-ene copolymers at 110° and 35 atm;[76] regenerated catalyst was more active than fresh catalyst[10]. Similar results were obtained with a $ZrO_2-SiO_2-Al_2O_3$ cracking catalyst[77].

The patent literature describes aluminosilicate catalysts, containing 0.5–20% Al_2O_3, for the polymerisation of olefins[62,78-86] and catalysts containing Zn, Zr, Be, Mg, Mn, Ti, Cd, Fe, Cr, Cu, and Th (20–50%) as activators[10,87-92]. Zn and Tl deactivate an aluminosilicate catalyst for isobutene polymerisation[69].

2. Semiconducting Metal Oxides

Oxides of Group II metals. Over ZnO propyl chloride forms propene and its liquid polymers at 250° and 36 atm, apparently with intermediate formation of the biradical $CH_3\dot{C}H\dot{C}H_2$.[93] At 100° and 26–73 atm isobutyl chloride gave isobutene and its dimers and trimers[94]. Direct polymerisation of propene and but-1-ene in the presence of ZnO and CaO takes place at 150° under u.v. irradiation[95].

Oxides of Group III metals. Alumina containing 10% of rare-earth oxides (Ce, Nd, Gd, Sm, Dy, Er, Yb) has been used for the polymerisation of ethylene[96]. The most active oxides are those of Dy and Yb, the oxides of Nd and Gd being slightly less active. Cerium oxide is inactive. At 240° and 140 atm total pressure ethylene gave solid polymers when $LiAlH_4$ was added as activator. Only liquid polymers were obtained when triisobutylaluminium was added. TiH_4 did not activate the process at all. With these catalysts there was no polymerisation of propene.

Oxides of Group IV metals. The oxides of Ti,[21,25] Zr,[10,21,25] and Th[9,21] polymerise C_{3-5} olefins at 100°–600°; u.v. light promotes the reaction[95]. Ethylene polymerises at 140° and 70 atm in the presence of TiO_2 activated with LiH.[25] When hexan-1-ol and 2-ethylhexan-1-ol are dehydrated over ThO_2 at ~400°, the polymer is obtained in 10–15% yield; C_{6-8} olefins themselves are 3–4% polymerised[14].

Oxides of Group V metals. Solid polymers of α-olefins have been obtained[97-100] using oxides of V, Nb, and Ta on various carriers (γ-Al_2O_3, SiO_2,[97-101] MgO, TiO_2, ZrO_2, and aluminosilicate[101]) activated with hydrogen at 250°–350° or by addition of alkali and alkaline earth metals and their hydrides, hydroborates, or hydroaluminates. The oxides of V and Nb were the most active, and the oxide of Ta less so[102]. Ethylene and propene have

been polymerised at 75°–325° and 14–350 atm in a diluent (toluene, xylene, or decalin).

Oxides of Group VI metals. *Chromium oxide* alone is not very active in the polymerisation of gaseous olefins[9,103], but propene is vigorously polymerised to liquid hydrocarbons at 310° and 150 atm in the presence of Cr_2O_3 on Al_2O_3. Steam intensifies the reaction. At 185 atm there is ~95% reaction[104]. The liquid product contains a mixture of dimers[105]. A mixture of ethylene and higher olefins at 850° in the presence of aluminosilicate containing 3.4% Cr_2O_3 gave mainly benzine[73,106].

The industrial conversion of olefins to solid polymers[107-114] is of great interest. One of the catalysts used is chromium oxide on aluminosilicate[102,105,107,115-142], the optimum amount being 2–5%.[107,118,119,131-134] The best carrier is an industrial synthetic aluminosilicate catalyst with $SiO_2 : Al_2O_3 = 9 : 1$;[107,118,122] also useful are metallosilicates[123], natural aluminosilicates[118], activated carbon[120], and oxides of Si, Al, Zr, and Th.[103,105,118,126,129,134,139] Solid polymers are given by all α-olefins containing not more than 8 carbon atoms and in which there is no branching closer to the double bond that the fourth carbon atom[107,128,129,132]; an exception to this rule is 4-methylpent-1-ene, which gives a solid polymer[107]. Copolymerisation of olefins can also be accomplished[115]. Polymerisation can be effected both in the vapour phase at 83°–250° and atmospheric pressure[119,128,133] and in the liquid phase in a diluent at 55°–250° and pressures up to 42 atm[107,114-122,129,130,133-140,142] with a fixed or suspended catalyst. The olefin must be carefully freed from H_2O, O_2, CO_2, and CO. The yield and molecular weight of the polymer are greatly dependent on the composition, method of preparation and content of the catalyst in the solution, the temperature and duration of its activation, the reaction temperature and pressure, and the time of contact. Chromium oxide catalysts do not require preliminary reduction or addition of activators, although the latter improve their properties[102,143-153]. The activators may be alkali and alkaline earth metals[102,143-145,149,152] and their oxides[150], hydrides, and hydroborates[102,152,153], aluminium trialkyls[120], alkali metal hydroaluminates[102,143-145,152], alkaline earth metal carbides[151], sodium pentyl[148], and certain metals and their mixtures (La, Ce, Nd, Th, and U).[153] A catalyst prepared by impregnating synthetic aluminosilicate with CrO_3 solution and treating with air at > 300° contains mainly Cr^{VI} and is inactive[103]. At 350° the Cr^{VI} is partially converted to Cr^{III} and at 480°–500° the ratio $Cr^{VI} : Cr^{III}$ is 1.55–3.2[118] – these are the most active catalysts. Above 600° this ratio decreases and the activity again falls: increasing the activation temperature from 450° to 600° gives a polymer of lower molecular weight[118,154]. If the aluminosilicate is impregnated with chromium nitrate solution, the catalyst is activated at a higher temperature (550°–600°) and with a faster flow of air[103,118]. The optimum concentration of catalyst is 2–3%.

Electron paramagnetic resonance has shown that in aluminochrome catalysts [Al_2O_3–Cr_2O_3 (Ed. of Translation)] containing less than 3–4% of chromium oxide the Cr_2O_3 microcrystallites consist of 3 or 4 atomic layers bonded to the carrier, the surface layer of microcrystals containing a considerable number of Cr^{3+} ions[155].

The reaction temperature and the molecular weight of the polymer decrease with increasing molecular weight of the olefin. The optimum reaction temperature is 150°–180° for ethylene and 105° for propene[107,118-120]. When the reaction temperature for the polymerisation of ethylene was increased from 110° to 170°, the molecular weight of the polymeric product fell from 100 000 to ~25 000[107] and its yield decreased by a factor of 1.6.[118,154-159] The yield and molecular weight of the polymer increased with increasing pressure over the range 6–60 atm.[107,118,154]

Oxides of Mo and W deposited on Al_2O_3 and *tungsten oxide* on activated carbon are active in the conversion of propene to a mixture of isohexenes[73,105]. Isobutene is converted to dimers and trimers at 200° over MoO_3/Al_2O_3, and at 300°–450° polymerises with subsequent dehydrocyclisation of the reaction products[160]. Ethylene polymerises to solid polymers over a hydroforming catalyst or over MoO_3 deposited on γ-Al_2O_3 (1 : 4)[161-165], TiO_2, ZrO_2,[166] or on aluminosilicate[167]. Temperatures of 75°–325° and pressures up to 350 atm give polymers of molecular weight up to 50 000. Preliminary treatment of the Mo catalyst with acetylene prevents coke formation and increases the useful life of the catalyst[168]. Reaction takes place in the vapour phase or in a diluent[146]. Reduction of pressure in the range 55–70 atm and increase of temperature in the range 100°–400° increases the yield of liquid products. Even at 320° liquid polymers are formed almost exclusively[169]. Catalysts based on oxides of Mo, W, and U are treated with hydrogen and activated by adding Li, Na, CaH_2,[102] or CaC_2,[170] which reduce the catalyst, remove catalyst poisons[152], and also participate directly in the reaction[102,114].

Oxides of Group VIII metals. *Oxides of Pd and Fe.* Ethylene has been polymerised to high molecular weight polymers using Pd oxide on aluminosilicate activated by hydrogen above 600°[171] and Fe oxides on aluminosilicate activated by air at 510°.[172]

Nickel oxide does not polymerise ethylene[173,174] or but-1-ene[175] at 270°–300°. Ethylene decomposes explosively at 330° and 49 atm in the presence of a $4NiO–2Al_2O_3–CuO$ catalyst. At 500°–515° pyrolysis gas gave traces of liquid polymers; under these conditions the use of cobalt oxide produced soot, H_2, and CH_4.[9] Nickel oxide deposited on silica gel[176-178], silicate glass[179], kieselguhr[174,180-183], active carbon[174,184], thorium dioxide[185], and synthetic aluminosilicate[173,177,178,181,184,186-189] is active. The earliest studies in this field were by Sokolov and coworkers (see Kazanskii *et al.*[177]). The polymerisation of ethylene in the presence of NiO on various carriers was studied in detail by Eidus and Kazanskii and their coworkers[175,177,190-198]. The deposition of NiO on technical samples of silica gel by precipitation or impregnation with solutions of nickel salts gave inactive catalysts[177-190], with the exception of NiO on KSK silica gel, which produced 20–30% dimerisation of ethylene and 7–11% polymerisation to liquid products. Technical silica gels contain up to 1.5% Al_2O_3,[199,200] and this apparently causes the activity of the catalyst, which, however, rapidly declines[190]. In fact a small amount of Al_2O_3 has a strong promoting action on an NiO–KSK silica gel catalyst in the polymerisation reaction, both at atmospheric pressure[177,191] and at 135 atm.[176] The selective action of the NiO–KSK silica gel catalyst promoted with Al_2O_3 in respect of ethylene dimerisation is considerably increased by adding oxides of Cu, Ag, Zn, Ba, and Mn; the addition of oxides of Ag, Ca, and Ba reduced the total activity of the catalyst, and the addition of oxides of Ag, Ca, and Mg greatly reduced its stability. Addition of oxides of Cu, Zn, Mn, Mg, or Th did not affect the activity[176,192].

Nickel oxide on synthetic aluminosilicate is the most active and stable catalyst for the polymerisation and copolymerisation of olefins at temperatures from room temperature to 300° and pressures of 1–40 atm.[177,181,184,186,187,193,201] The optimum content of NiO is 4%.[173,177,201] Ethylene gives predominantly the dimer at 275°–300° and atmospheric pressure with a time of contact of 2.5 sec over this catalyst[194]. The rate of polymerisation decreases with increasing molecular weight of the olefin[181,187]. In the presence of an equal volume of H_2 ethylene is 97% converted to a mixture of true polymers, ranging from butenes to dodecenes and higher polymers, at 40° and 20 atm,[201] while at 70°–93° and 41 atm propene mixed with propane gives a liquid polymerisate in a yield directly proportional to the propene concentration. The life of the catalyst is increased several times by carrying out the polymerisation of olefins in the presence of diluents[201]. Hydrogen acts as a diluent only at comparatively low temperatures. At 260°–270° H_2 promotes polymerisation[186]. Over an impregnated NiO–aluminosilicate catalyst at the optimum temperature of 275° ethylene gives as the main product either the dimer (at atmospheric pressure) or liquid hydrocarbons (at 30 atm).[197] Increase of the pressure to 30 atm and of the temperature to 275° favours the formation of liquid hydrocarbons. The liquid polymerisate obtained from ethylene at 275° and elevated pressure comprises ~16–32% hexenes, ~18–23% octenes, 25–35% higher hydrocarbons, 12–24% "odd" polymers (C_5, C_7, and C_9 hydrocarbons), and 4–11% semi-solid residue boiling above 300°.[198] The main constituents were 3-methylalk-2-enes, with lesser amounts of 2-methylalkenes, dimethylalkenes, and the corresponding alkanes[198]. At atmospheric pressure the main product was the dimer but-2-ene, with lesser amounts of liquid hydrocarbons comprising ~45% hexenes, ~15% octenes, ~15% "odd" polymers, and ~25% higher hydrocarbons containing 2-methylalk-2-enes and a large quantity of α-olefins[196]. Gaseous olefins polymerise at 0°–140° and 1–45 atm over an NiO–kieselguhr catalyst[174,178–183,202–204]. The activity of this catalyst is due to dehydration during its activation. In the presence of a diluent ethylene polymerises to solid polymers at 100°–180° and 55–70 atm over an NiO catalyst on active carbon previously reduced by H_2 or activated by NaH or $LiBH_4$.[169,170,205,206].

Oxides of metals of Groups II–VIII are thus weak catalysts for the polymerisation of olefins; their deposition on carriers (metal oxides, aluminosilicates) produces active catalysts, and the polymerisation may produce either low- or high-molecular-weight polymers. Isoolefins (isobutene) are the most vigorously polymerised over natural and synthetic aluminosilicates, over a wide range of temperatures and pressures. Normal olefins require most severe conditions, and ethylene does not polymerise at all. The composition of the reaction products is similar to that of the polymerisates obtained in the presence of acids. Over transition metal oxide catalysts on aluminosilicates as carriers it is the normal olefins which are generally polymerised, and ethylene most vigorously of all. Low-molecular-weight polymerisation of olefins provides polymers which are multiples of the initial olefin. High-molecular-weight polymers are obtained from these catalysts after activation with hydrogen or special activators, at elevated temperatures and pressures, while in the presence of aluminosilicates high-molecular-weight polymerisation takes place at atmospheric pressure and ~ -80°. Over NiO catalysts the polymerisation of ethylene can be controlled so as to produce predominantly either the dimer or high-molecular-weight polymers.

II. ISOMERISATION OF OLEFINS

In the presence of metal oxides olefins may isomerise with shift of the double bond or change of the carbon skeleton, or they may undergo *cis–trans*-isomerisation. These processes are reversible, and depending on the conditions and the oxide used may proceed simultaneously or selectively[207].

1. Non-Conducting Metal Oxides

Aluminium oxide catalyses the shift of the double bond in the olefins produced by the dehydration of alcohols[27,208–214]. Over carefully purified Al_2O_3 butan-1-ol gives only but-1-ene[215]; but-2-ene is formed when the alumina contains acidic impurities and also when the temperature is raised[213,216,217], above 400° isobutene also being obtained[17,208,218–220]. At 150°–400° n-pentyl[221] and isopentyl[222–225] alcohols gave a mixture of pentenes differing in the position of the double bond. In the dehydration of a series of higher alcohols[14,226–229] some results indicated a displacement of the double bond and carbon-skeleton isomerisation, while according to others[19,224,229–231] there was no isomerisation or only a shift of the double bond. Over Al_2O_3 activated at 450° there is rapid isomerisation of n-butenes[16,17,232] and of pent-1-ene to pent-2-ene,[23,233] while over Al_2O_3 activated with HF there is carbon-skeleton isomerisation also[23,234]. The equilibrium composition of the isopentene mixture is reached in ~12 h at 250°–400°.[233,235–237] Shift of the double bond in hexenes of various structures takes place at 80°.[237] At 190°–440° there is also carbon-skeleton isomerisation, although equilibrium is not reached[14,226,238]. The calculated and experimental equilibrium compositions of hexenes at 100°–480° have been given[14,234,238,239]. Neohexene does not react at all[227]. Aluminium oxide treated with HCl or HF[22,207,234,238,240–242] or containing acidic additives (ammonium sulphate, kieselguhr)[226] caused the isomerisation of a series of C_{6-16} olefins at 190°–340°; cracking and polymerisation occurred to a marked degree. As a rule n-olefins are converted to the monomethyl-substituted isomers with the methyl group at the double bond, and then to dimethyl substituted isomers, the second methyl group being generally in position β with respect to the first. To a certain extent there is a shift of the double bond and the methyl group to the centre of the main carbon chain. In the case of C_{12-16} olefins the di- and tri-methyl substituted isomers are converted to monomethyl substituted isomers. Shift of the double bond in olefins to the centre of the molecule has been observed with Al_2O_3 on pumice at 330°–380°,[243] γ-Al_2O_3 containing metallic Na at 0°–100°,[244] and Al_2O_3 treated with HF at 300°–600°.[245] Under the same conditions Al_2O_3 can produce carbon-skeleton isomerisation of n-olefins[246,247].

Silicon dioxide in the form of technical silica gel can promote equilibration in the case of n-butenes even at 200°,[27,238] with partial formation of isobutene and pentenes[33]. Raising the temperature to 380° produces carbon-skeleton isomerisation. Hex-1-ene[22], *trans*-4-methylpent-2-ene, 3,3-dimethylbut-1-ene, 3-methylpent-2-ene, and 4-methylpent-1-ene[226] are not isomerised over silica gel at 300°–340°; however, silica gel becomes markedly active when treated with HCl[22] or irradiated with fast neutrons[248]. Equilibrium in the double bond displacement reaction with olefins of the type $RR'C{=}CH_2$ and $RCH{=}CR'R''$ is reached even at 25°, and the more rapidly the greater the ratio of silica gel to olefin[226,249]. Over

SiO_2 at 400° oct-1-ene is converted mainly to mixed methylheptenes[250].

Aluminosilicates. *Clays* produce isomerisation when isobutyl alcohol is dehydrated over them[251]. Butan-1-ol gives only but-2-ene over a clay–infusorial earth catalyst[252], a mixture of three butenes over gumbrine and askanite at 400°–450°,[253,254] and a mixture of n-butenes over bentonite and Uchkekensk clay†[255,256]. In the presence of Glukhov clay and Floridin n-butenes (diluted with steam to suppress polymerisation) are 6–7% converted to isobutene at 294°.[257] At 260°–335° hex-1-ene is converted to methylpentenes over activated clay[258,259]. The dehydration of 4-methylpentan-2-ol and heptan-2-ol over Floridin at 300°–385° gives mixed hexenes and heptenes respectively, differing in the position of the double bond[224]. At 160°–170° 3,3-dimethylbut-1-ene and 4,4-dimethylpent-2-ene undergo irreversible isomerisation to 2,3-dimethylbut-2-ene and 2,3-dimethylpent-2-ene respectively[260].

Permutite produces carbon-skeleton isomerisation of butenes and pentenes at 400°[261] and of hexenes at 335°.[22]

Andalusite converts pent-1-ene at 300°–550° mainly to pent-2-ene and only to a slight extent to methylbutenes[262].

Bauxite activated at 700° produces an equilibrium mixture of n-butenes at 250°–550° from mixtures of various composition[220,263-265].

Synthetic aluminosilicates produce isomerisation of olefins[29,75,77,263,266-270]. Shift of the double bond in n-butenes takes place at a rapid rate even at 100°–150°; equilibrium between the n-butenes is readily established at 270°–500°. At 400°–600° up to 40% of isobutene is formed, with simultaneous polymerisation and cracking[75,77,267]. Under the same conditions the reverse isomerisation of isobutene to n-butenes takes place, but without reaching equilibrium. A stereospecific isomerisation of but-1-ene to but-2-ene has been observed at 65°–66°; at low degrees of conversion the unstable *cis*-but-2-ene is the main product. Irradiation of the catalyst with γ-rays or neutrons reduces its activity, but does not affect the stereospecificity[271]. At 400° n-pentenes are more than 50% converted to methylbutenes[75]. The equilibrium compositions of pentenes[77,267,272] and hexenes[22,240] at various temperatures have been determined. As a result of hydrogen redistribution in the isomerisation of C_{6-8} olefins[207,241,273,274] the thermodynamically unstable as well as the stable isomers become saturated. The reactions of n-olefins over synthetic aluminosilicate catalysts have been studied by Naragon[240].

Among other metal silicates, those of magnesium ($2MgO.SiO_2$) and zinc ($2ZnO.SiO_2$) convert pent-1-ene at 300°–500° into a mixture of pent-2-ene and 2- and 3-methylbut-1-enes[262]; magnesium silicate is more active than zinc silicate, and the latter more active than andalusite.

2. Semiconducting Metal Oxides

Oxides of Group II metals. At 450° *beryllium oxide* produces shift of the double bond and carbon-skeleton isomerisation; hept-1-ene is converted predominantly into methylhexenes[250,275]. At 100° and 14 atm but-1-ene is 90–95% isomerised to but-2-ene in the presence of activated *magnesium hydroxide*, with simultaneous formation of liquid hydrocarbons. Pentenes are also isomerised under these conditions[276]. There is a shift of the double bond in butenes over *calcium oxide* at 600°.[232,264,265] *Zinc oxide* is inactive below 450°,[93,277-279] but at 450°–650° it produces shift of the double bond in olefins, and above 650° dehydrogenation and decomposition occur[279]. The addition of 1% Ga^{3+} to ZnO does not markedly affect its catalytic properties, but addition of 1% Li^+ completely suppresses them.

Oxides of Group IV metals. Over *thorium dioxide* at 385° but-1-ene, as such or at the moment of its formation from butan-1-ol, isomerises to but-2-ene, with some polymerisation and decomposition[232,233,280]. Hexenes and heptenes also isomerise[232,233]. n-Olefins are converted to isoolefins over thorium and zirconium oxides at 332°–555°.[246,281]

Oxides of Group V metals. Mutual interconversion of hept-1-ene and hept-2-ene without change of the carbon skeleton occurs at 400°–480° over *vanadium trioxide* deposited on Al_2O_3 (1 : 10).[282]

Oxides of Group VI metals. But-1-ene is about 80% converted to but-2-ene at 250°–260° over black *chromium oxide* (CrO_2).[283] In the production of aromatic hydrocarbons from isoolefins over Cr_2O_3 at 474° the isoolefins are first isomerised to n-olefins[14,284]. The chromium oxides may be deposited on an aluminosilicate carrier[232,233,285].

Molybdenum oxide produces shift of the double bond in hexenes at 400° and 140 atm; no carbon-skeleton isomerisation was observed[286,287].

Oxides of Group VII metals. Manganese oxide on Al_2O_3 shifts the double bond in isopentenes[233].

Oxides of Group VIII metals. *Nickel oxide* promotes polymerisation and decomposition to a considerable extent, and it is therefore not considered to be an effective catalyst for the isomerisation of olefins[9,233,278]. NiO on Al_2O_3[233] or aluminosilicate is an active catalyst for shift of the double bond in n-butenes at 270° and for carbon-skeleton isomerisation of ethylene polymers at 275°.[198] An NiO–glass catalyst does not isomerise butenes[175]. The activity of NiO containing Cr_2O_3 is directly proportional to the Cr_2O_3 content, and is due to the presence of nickel chromate as a new phase[278].

Cobalt and iron oxides on aluminium oxide produce shift of the double bond in isopentenes at 300°–370°.[233]

In the isomerisation of olefins the most active catalysts are thus the non-conducting oxides of metals of Groups II–VIII. Over these the reaction proceeds to equilibrium over a wide range of temperatures from room temperature to 500°. Below 150° there is only *cis–trans* isomerisation and shift of the double bond towards the centre of the molecule; this last reaction takes place most readily with isopentenes having a side chain at the double bond. At 250°–500° carbon-skeleton isomerisation also occurs. Over Al_2O_3 carbon-skeleton isomerisation of C_5 and higher olefins proceeds practically to equilibrium, but over aluminosilicates this does not happen, because redistribution of hydrogen produces some hydrogenation of the thermodynamically unstable olefins. Carbon-skeleton isomerisation over non-conducting metal oxides proceeds stepwise: normal olefins are converted to the monomethyl substituted isomers, predominantly with the methyl side chain at the double bond, and then the dimethyl substituted

† Chem. Abs. translates this as "bentonite", Chem. Abs., 42, 1562 h (1948) (Ed. of Translation).

isomers are produced. Typically, higher hydrocarbons undergo "straightening" of the carbon chain, but at a low velocity. 2- and 3-methylalkenes and 2,3- and 2,4-dimethylalkenes with the double bond at the "tertiary" carbon atom undergo isomeric conversions at a reduced rate.

Over semiconducting oxides of metals of Groups II–VIII only shift of the double bond of C_{4-8} olefins takes place at 300°–650°, sometimes under pressures of up to 140 atm. Oxides of Group II–IV metals can be used as isomerisation catalysts without a carrier, but oxides of Group VI–VIII metals require a carrier (Al_2O_3, aluminosilicates), since when used alone they produce vigorous decomposition and polymerisation of olefins.

III. DECOMPOSITION OF OLEFINS

The decomposition of olefins over metal oxides may proceed with rupture of C–C and C–H bonds simultaneously, and this is typical of the high-temperature decomposition when the composition of the final reaction products is little affected by the structure of the molecule (catalytic cracking). This type of reaction is used for the production of high-octane motor fuels[288,289] and C_{3-4} olefins employed as starting material for industrial petrochemical synthesis[290]. Another type of olefin decomposition reaction, which is used to obtain pure olefins, such as isobutene[291-295], occurs by rupture of C–C bonds and is formally the reverse of polymerisation, *i.e.* depolymerisation[287]. This is a low-temperature process, the nature of the products depending on the structure and molecular weight of the initial olefin. Lebedev and Koblyanskii have shown that the polymerisation of olefins over Floridin, which commences from ~200°, is complicated by depolymerisation of the resulting polymers[45,46].

A. CATALYTIC CRACKING

1. Non-Conducting Metal Oxides

Aluminium oxide and silicon dioxide separately are not very active in the cracking of olefins[23,296,297]. Treatment of aluminium oxide with HF [23] or HCl [242] or addition of even hundredths of a per cent of Al_2O_3 to SiO_2 [240,296,297] produces highly active cracking catalysts. Natural clays are also active[258,298].

Synthetic aluminosilicates. Over synthetic aluminosilicates olefins of various structures and molecular weights are cracked at 350°–450° to form C_{1-4} hydrocarbons and liquid products consisting of olefins and aromatic and saturated hydrocarbons[75,77,266,267-269,299-302]. Fig. 1 shows the conversion of normal olefins at 400° over a synthetic aluminosilicate catalyst as a function of the molecular weight.

2. Semiconducting Metal Oxides

But-1-ene undergoes vigorous dehydrogenation and decomposition at 615° over *zinc oxide* containing 1% Ga in a nitrogen atmosphere, producing C_4H_6, C_3H_6, and C_2H_4 in the ratio 2 : 2 : 1.[279] Isobutene is unchanged under these conditions, while 3-methylbut-1-ene and 2-methylbut-2-ene are dehydrogenated and lose the methyl group.

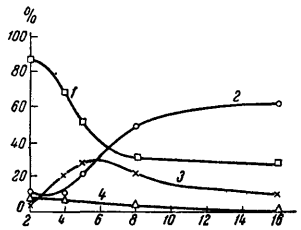


Fig. 1. Distribution of conversion products of n-olefins at 400° and space velocity 6.8 moles per litre of catalyst per hour, as a function of molecular weight:
1) unreacted olefins; 2) cracking products boiling below the initial olefin; 3) polymerisation products; 4) coke formation.
y axis: percentage conversion of olefin;
x axis: number of carbon atoms in the initial olefin.

At 500°–515° *nickel and cobalt oxides* degrade C_{2-4} olefins to methane and carbon[9].

B. LOW-TEMPERATURE DECOMPOSITION

Unlike catalytic cracking, low-temperature decomposition takes place at 150°–200°, but only with olefins of a certain structure and only over aluminosilicates[303].

Floridin and clays depolymerise olefin polymers at low temperatures[36-39,304] With polymers of isobutene and the isopentenes the reaction commences at a temperature as low as 50° and proceeds vigorously at 50°–250°; [41,43-46,305] polymerisation of the monomers and dimers takes place simultaneously, together with some redistribution of hydrogen. The depolymerisation is easier the higher the molecular weight: diisobutylene is the most stable, while triisobutylene decomposes practically completely into diisobutylene and isobutene[296,305,307]. Dimers of isobutene and its copolymers with n-butene are depolymerised over clay[308,309] and Volga kieselguhr (Volga opoka)[310], the yield of isobutene increasing with temperature over the range 200°–428°.

Synthetic aluminosilicates are sometimes more active[310] and sometimes less active[308,309] than natural clays in the depolymerisation of diisobutylene. At 367° triisobutylene is 70% depolymerised to isobutene[299]. Only olefins with two or more alkyl side chains in the β-position relative to one another undergo low-temperature decomposition[303,310].

Over aluminosilicates C_{2-12} olefins are cracked at 350°–500°, mainly with rupture of C–C bonds; isomerisation, aromatisation, polymerisation, and hydrogen redistribution take place at the same time. The ease of decomposition increases with the molecular weight of the olefin and the reaction temperature. Isoolefins react more readily than their normal isomers. At 150°–250° olefins with alkyl

side chains in the β-position relative to one another undergo decomposition, and the more readily the greater the number of such side chains in the molecule. Al_2O_3 and SiO_2 do not produce cracking of olefins even at 300°–450°, but they become active in this respect after treatment with mineral acids (HF, HCl). The semiconducting metal oxides which have been studied require higher temperatures (~500°–600°) to produce decomposition of olefins.

IV. REDISTRIBUTION OF HYDROGEN

The formation of saturated hydrocarbons takes place in the polymerisation[11,12,28,58,74], isomerisation[207,241,273,274], and cracking[75,77,258,262,266-269,298,299,301,311-313] of olefins over aluminosilicates. This reaction is sometimes used to improve the anti-detonation properties and stability of fuels[290,314-319].

1. Non-Conducting Metal Oxides

Aluminium oxide and silicon dioxide. Neither aluminium oxide nor silica gel is active in the redistribution of hydrogen in olefins. Al_2O_3 activated with HCl is an active catalyst for the refining of highly unsaturated petroleum fuels[320,321].

Aluminosilicates. Over *Floridin* saturated hydrocarbons are produced in the depolymerisation of dipentenes[41]. Alkanes are obtained from cracking petrol at 260° over activated clay[258,311,322-324]. Over *synthetic aluminosilicates* the reaction takes place with butenes at 300°–400°[320] and with oct-1-ene and 2-ethylhex-1-ene at 250°.[324] The reaction proceeds selectively[267,301,311,324] and most readily with olefins containing a "tertiary" carbon atom at the double bond, the hydrogen donors being either hydrocarbons [acyclic hydrocarbons? (Ed. of Translation)], which are converted to coke-like condensation products[207,301,311,325,326], or naphthenes[320]. Molecular hydrogen, like nitrogen, acts as a diluent[207,267]. The redistribution of hydrogen between naphthenes and olefins at 300°–400° is most vigorous on a catalyst containing 75% SiO_2.[320] Isoolefins become saturated considerably more readily than normal olefins. Coke is formed mainly from the olefin.

2. Semiconducting Metal Oxides

Up to 20–50% of ethane is produced in the dehydration of ethanol over *titanium dioxide* at 360°–400°.[327] *Chromium oxides* deposited on Al_2O_3 are inactive even at 400°.[267] The polymerisation product of ethylene at 275° and 1–30 atm over an NiO–aluminosilicate catalyst contains up to ~50% of saturated hydrocarbons, predominantly of iso-structure[198].

The data reviewed in this section show that the redistribution of hydrogen in olefins or between olefins and naphthenes occurs mainly in the presence of aluminosilicates. This reaction is important in the refining of unsaturated petroleum fuels and is best conducted at 250°–450° and 1–8 atm. Olefins with a tertiary carbon atom at the double bond are the most readily saturated, so that isoparaffins accumulate in the reaction products, and this improves the anti-detonation properties of the motor fuels.

V. HYDROGENATION OF OLEFINS, *ortho–para*-HYDROGEN CONVERSION AND DEUTERIUM–HYDROGEN EXCHANGE

Several reactions characteristic of metal catalysts also take place over metal oxides: hydrogenation, H–D exchange, and o–p-H_2 conversion. These reactions apparently take place on oxide films on the metals[328,329]. Hydrogenation over oxide catalysts proceeds at 250°–500°, when the oxide may be partially reduced to the metal, so that it is difficult to decide whether the hydrogenating activity is due to the metal or oxide. o–p-Hydrogen conversion and deuterium exchange over oxides take place at temperatures from -200° to 0°, when there can be no reduction of oxide to the metal.

A. HYDROGENATION OF OLEFINS

Oxides of Group I metals. Among these *copper oxide* possesses hydrogenating activity; in its presence ethylene and hydrogen produce ethane and a little methane at 180° and 60 atm. Trimethylethylene is almost completely converted to isopentane at 300° and 100 atm.[330]

Oxides of Group II metals. ZnO and MgO are inactive at 400° and atmospheric pressure[331]. ZnO is deactivated by small amounts of water and is activated by prolonged heating in a vacuum at 450°. Polymerisation and decomposition also occur in addition to the hydrogenation[332]. Irradiation of ZnO with γ-rays reduces its hydrogenating activity[333].

Oxides of Group III metals. Ethylene is ~80% hydrogenated to ethane at 500° over *aluminium oxide* activated at 400°–800°.[334] SiO_2 deactivates Al_2O_3. The hydrogenating activity of Al_2O_3 is due to deformation of its surface because of dehydration during the heating[335-341]. However, because of the high temperature used the hydrogenation may be only semi-catalytic, *i.e.* without activation by the hydrogen catalyst[339].

Oxides of Group IV metals. Ethylene is hydrogenated slowly over *titanium dioxide* at 300°–400°.[327,331]

Oxides of Group V metals. Isobutene, hex-1-ene, and oct-1-ene are 80–98% hydrogenated at 300°–400° over *vanadium trioxide* on Al_2O_3, this being accompanied by isomerisation[342-346].

Oxides of Group VI Metals. Olefins are hydrogenated at 350°–400° and 1–49 atm over amorphous *chromic oxide*[342,343,347], and at 200°–350° over thoroughly purified Cr_2O_3.[343] Crystalline Cr_2O_3 is inactive[348,349]. Addition of potassium and treatment with air reduce the activity of Cr_2O_3.[285] Its activation by treatment with hydrogen has been ascribed to partial reduction[350]:

$$Cr_2O_3 + H_2 \rightarrow Cr_2O_3 \cdot H_2 \rightarrow (CrO_2) \cdot H_2O. \quad (1)$$

Ethylene is hydrogenated at 184° over an $MnO-Cr_2O_3$ catalyst, with simultaneous vigorous decomposition[351]. Over a $Cr_2O_3-Al_2O_3$ catalyst hydrogenation proceeds to the extent of 94% at 200°;[334,352] the rate of hydrogenation of mixed n-butenes over this catalyst is given by the equation[353]:

$$W = kP_{H_2}P_{C_4H_8}^{0.5}. \quad (2)$$

An MoO_3 catalyst prepared from ammonium nickelomolybdate was very active, because of the formation of metallic

nickel; a catalyst prepared from ammonium phosphomolybdate and paramolybdate had a low activity[347]. The hydrogenation of ethylene over an MoO_3–aluminosilicate catalyst at 150°–350° and 50–400 mm Hg apparently proceeds by a radical-chain mechanism, and at high degrees of conversion its rate is reduced by the formation of ethylene polymers[354,355].

Oxides of Group VIII metals. The hydrogenation of ethylene to ethane at 130°–140° and 60 atm over *nickel oxide* is accompanied by considerable decomposition[330].

B. *ortho*–*para*-HYDROGEN CONVERSION

This reaction takes place at 20°–86°K and ~1.05 atm over Gd_2O_3, CeO_2, NiO, 2% paramagnetic Fe_2O_3 on porous glass, Fe_3O_4, 20% Cr_2O_3 on Al_2O_3, 15% paramagnetic Fe_3O_4 + 9.3% Cr_2O_3 on Al_2O_3, MnO_2,[356,357] and ZnO.[358-360] Of iron oxides the most active at -195° is the antiferromagnetic α-Fe_2O_3.[361] Even more active are the hydroxides of certain elements with an incomplete 4*f*-electron shell (hydroxides of Pr, Gd, Tb, and Dy) or 3*d*-electron shell (hydroxides of Cr, Mn, Fe, Co, and Ni);[362] this is ascribed to dilution of the paramagnetic ions. The concentration [high concentration? (Ed. of Translation)] of these ions in Cr_2O_3, NiO, and Fe_2O_3 is the cause of their antiferromagnetism and reduced catalytic activity.

C. DEUTERIUM–HYDROGEN EXCHANGE

1. Non-Conducting Metal Oxides

Aluminium oxide. Over heat-activated γ-Al_2O_3 H–D exchange takes place at temperatures from -124° to +200°,[334,337,362] the activity being determined by the degree of dehydration. Addition of sodium Al_2O_3 does not promote H–D exchange[363], but addition of NaH [364] or irradiation with γ-rays, α-particles, or neutrons[365] does favour the exchange. Adsorption and deuterium exchange take place when two molecules are present on one active centre[366].

Aluminosilicates. Deuterium exchange takes place at 150°–350° in the presence of *synthetic aluminosilicates*; its rate depends on the SiO_2 content and the activation and reaction temperatures[334,367,368] (Fig. 2). Above 350° there is considerable saturation, polymerisation, and cracking in addition to the deuterium exchange[367]. The activity of silica gel, quartz, and synthetic aluminosilicates in deuterium exchange at room temperature is greatly increased by irradiating them with γ-rays or neutrons[365].

2. Semiconducting Metal Oxides

In their activity in deuterium exchange the oxides of Group II–VIII metals lie in the series[4,350,358,359,369-371]:

$$WO_3 \gg FeO + Fe_3O_4 > ZnO > Al_2O_3 > ThO_2 > MgO > Cr_2O_3 > ZrO_2 > CeO_2 > > V_2O_5 > TiO_2, \quad (3)$$

and supported oxides in the series:

$$NiO + \text{kieselguhr} > Cr_2O_3 - Al_2O_3 > MoO_3 - Al_2O_3 > Cr_2O_3 - Fe_2O_3 - K_2CO_3 > WO_3 + + Al_2O_3 \gg \text{clay, bauxite} > \text{aluminosilicate}. \quad (4)$$

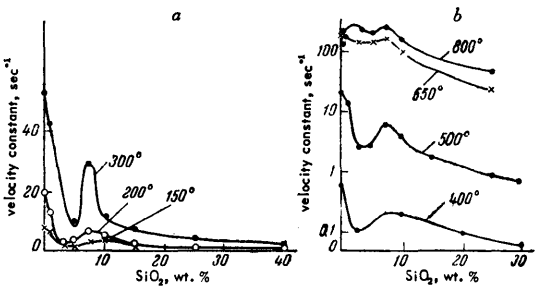


Fig. 2. Velocity constant of the deuterium–hydrogen exchange reaction as a function of the SiO_2 content of aluminosilicate and:
a) as a function of reaction temperature (activation temperature 500°); *b*) as a function of activation temperature.

The activity of oxides deposited on aluminosilicate decreases in the series:

$$ZnO > NiO > Cr_2O_3 > WO_3,\ UO_3,\ Fe_2O_3 > MoO_3\ . \quad (5)$$

Deuterium exchange over metal oxides is accelerated by raising the temperature to 350° and by treating the oxides with hydrogen. Traces of water completely deactivate them. The activity of ZnO when additives are present (Li_2O, Al_2O_3, and Ga_2O_3) changes in parallel with the conductivity[372-374].

At temperatures from -78° to 0° and 10 mm Hg the only active oxides are those of metals of approximately the same distance from the beginning and the end of the IVth Period (Cr_2O_3, Co_3O_4, and NiO) having some, but not too many, unpaired *d* electrons (Fig. 3)[375]. The low catalytic activity of oxides of metals at the beginning of the Period is due to the absence of *d* electrons; the oxides of metals in the centre of the Period have a stable $3d^5$ structure, while those of metals at the end of the Period have a full *d* shell. All these factors produce a slow rate of adsorption of hydrogen, and hence low catalytic activity.

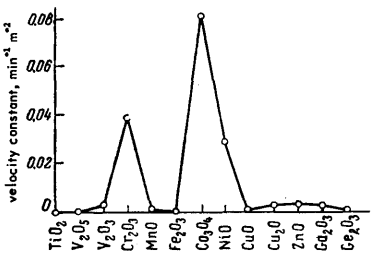


Fig. 3. Activity of the oxides of metals of the Fourth Period in deuterium–hydrogen exchange.

VI. NATURE OF THE CATALYTIC ACTIVITY AND THE MECHANISM OF THE REACTIONS OF OLEFINS IN THE PRESENCE OF METAL OXIDES

The difference in catalytic activity between non-conducting and semiconducting metal oxides in the olefin reactions reviewed reflects their differing abilities to activate C=C, C–H, and H–H bonds, and hence the mechanism of their catalytic activity is different. Thus over non-conducting oxides isoolefins are more readily polymerised than n-olefins, while with semiconducting oxides the reverse is true. The activity of semiconducting oxides in isomerisation, cracking, and disproportionation of hydrogen is less, but in hydrogenation, deuterium–hydrogen exchange, and *o–p*-hydrogen conversion it is greater than that of non-conducting oxides. This is seen from Fig. 4‡.

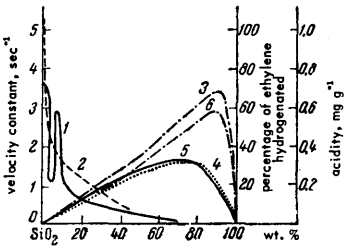


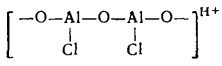
Fig. 4. Variation of velocity constants and acidity of the catalyst with SiO_2 content of a synthetic aluminosilicate:
1) hydrogenation of ethylene at 500°; [334] 2) deuterium exchange at 300° ($k \times 10$); [334] 3) polymerisation of propene at 200 ($k \times 10^3$); [376] 4) isomerisation of but-1-ene to isobutene at 340°; [320] 5) redistribution of hydrogen; 6) the acidity of the catalyst, as functions of the SiO_2 content of a synthetic aluminosilicate.

1. Non-Conducting Oxides

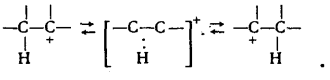
Aluminosilicates, aluminium oxide, and silicon dioxide have acidic properties [376-381] and a direct relationship exists between their catalytic activity and their acidity [28,29,297,381-387] determined by titration [29,388] with bases in non-aqueous solutions [376,377,389,390] and by the change of colour of indicators adsorbed on them [390]. Aluminosilicates react with solutions of carbonates [391,392] and with the Zerewitinoff reagent and hydrolyse sucrose [391]; they lose their activity when hydrogen ions are removed from their surface by exchange with alkali or alkaline earth metal ions [382] or ammonium ions [387] or when neutralised with organic bases [387,393,394].

The catalytic activity and acidity of aluminosilicates has been ascribed to the complex $(HAlSiO_4)_x$ which is present on the surface of inactive silicon dioxide [29,395] and which can liberate a proton. This complex is produced during the preparation of the catalyst by condensation of the alumina and silica gels produced by hydrolysis [376]. The replacement of silicon atoms (coordination number 4, valency 4) in the silicate lattice by aluminium atoms (coordination number 4, valency 3) produces an excess of electrons around the aluminium atoms, because of the known ability of the aluminium atom to accept an electron pair to complete the *p* orbital [29,376,381]. In an aqueous medium the electron pair is donated by water, and hydroxy-groups become components of the solid phase, as has been shown by isotope exchange of the oxygen of $H_2{}^{18}O$ with aluminosilicates [335]. When aluminosilicate catalysts are activated by heating, the surface loses water, with partial removal of protons [377,396,397]; in this case the activity of the aluminosilicates is apparently due mainly to the formation of an aprotic Lewis acid [391,398]. The formation of a new phase during the preparation of active aluminosilicates is demonstrated by their preparation from the inactive Al_2O_3 and SiO_2, the order of deposition of one oxide on the other not affecting the activity [399]. It has been shown [400-403] that the catalysts of maximum activity contain 30% Al_2O_3 and 70% SiO_2, which corresponds to the compound $Al_2O_3.4SiO_2$. X-Ray diffraction has also shown that the formation of a hydroaluminosilicate phase, similar to montmorillonite, during the preparation of aluminosilicates is a maximum with samples of composition $Al_2O_3.4SiO_2$. [404]

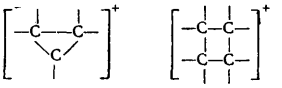
It has been suggested that the proton source in aluminosilicates and certain oxides activated with mineral acids is acid adsorbed on the surface [22,23]; for Al_2O_3 and HCl it has been shown that the acid is not only adsorbed by the oxide, but reacts with it to liberate a proton [207,405]:



Since aluminosilicates are acids and behave like strong mineral acids, their catalytic action has been explained by a mechanism involving the intermediate formation of a carbonium ion [23,29,75,77,267,297,396,406,407], as suggested by Whitmore for the polymerisation of olefins in the presence of acids [408-415]. Recently new forms of carbonium ion have been suggested. In a π-complex the proton occupies a position between the two carbon atoms of the double bond, as opposed to the classical structure of the carbonium ion (or σ-complex) with an open sextet of electrons [271,414-420]. The two forms may undergo interconversion:



In a π-complex the proton may be replaced by a methyl or other alkyl group:



The prevailing opinion, however, is that the reactions of olefinic hydrocarbons in the presence of acid catalysts are better explained by the classical carbonium ion structure [418,421,422], and this finds confirmation in the greatly differing affinities of the proton for the different carbon atoms of the double bond in asymmetric olefins [423-425].

Many investigators [14,218,253,254,284,426-428] have considered a molecular mechanism for the reactions of olefins in the

‡ A similar diagram has previously been published [383], but with certain inaccuracies in the scale when the curves were plotted. We have corrected these and amplified the diagram by including a curve showing the velocity constant for the isomerisation of but-1-ene to isobutene as a function of the SiO_2 content of the catalyst.

presence of aluminosilicates, the basis for this being L'vov's suggestion[429] of the intermediate formation of alkylcyclopropanes in the chemical reactions of olefins and alcohols.

2. Semiconducting Oxides

In their catalytic action semiconducting metal oxides are intermediate between transition metals and non-conducting metal oxides. The catalysis over semiconducting oxides proceeds at temperatures where there is marked lability of oxygen atoms on the surface; this is in accord, in particular, with oxygen exchange between $^{18}O_2$ and MgO, Al_2O_3, Cr_2O_3,[430] and ThO_2.[431] This may be the reason for the temporary deficiency of oxygen on the oxide surface, as a consequence of which its electronic structure alters. At present the catalytic activity of transition metal oxides is ascribed to their semiconductor properties and to the electronic arrangement of the *d* shell of their atoms[4,328,329,369,416,432-434].

Electronic theories of catalysis are based on the band theory of the solid state[435-438], which considers metal oxides as ionic solids[375], the outer free electrons of which belong to the whole crystal and move in the periodic field of the crystal lattice in various energy bands. The presence of free electrons on the surface of metal oxides is caused primarily by ionic defects in the crystal lattice, produced during the preparation of the catalysts or during the reaction by dissolution of the excess of metal or because of the excess of oxygen. In oxides with an excess of metal in the crystal lattice (*e.g.* ZnO, CdO, TiO_2, Al_2O_3, etc. — *p*-type semiconductors) there are either metal ions in the interstices or empty anionic positions with an equivalent number of free electrons. In oxides with an excess of oxygen (*e.g.* NiO, Co_3O_4, Cu_2O, CoO, etc. — *n*-type semiconductors) there are empty cationic positions and an equivalent number of holes. The electronic semiconduction in *n*-type semiconductors is due to electrons moving from donor impurity levels to the conduction band, and in *p*-type semiconductors, to the positive holes produced as a result of the transfer of electrons of the oxide to electron-acceptor impurity levels. The electrical conduction and catalytic activity of oxides can be controlled by the addition of metal cations of known ability to donate or accept electrons[439]. According to other results, the introduction of "foreign" cations into ZnO does not change the electronic structure of its surface, but does change the heterogeneity of the surface[440]. Defects are formed only on the surface of metal oxides, since the rate of diffusion of defects into the lattice at catalysis temperatures has a high temperature coefficient[432]. In oxide semiconductors of a third type (*e.g.* Cr_2O_3) the defects do not arise from impurities in the lattice, since they are stoichiometric in composition, but because of the transfer of electrons from the filled band to the conduction band, when they are excited[4,441] as a result of the reaction.

An important factor in the formation of structural defects is the participation of the carrier. Thus magnetic methods have shown that when deposited on γ-Al_2O_3 NiO has a higher concentration of holes, and hence a higher catalytic activity[442]. Similar results have been obtained for other oxides (Al_2O_3, MoO_2,[443] ZnO, BeO, Fe_2O_3 [444]). All these are the so-called "biographical" defects, which are retained at temperatures near absolute zero. Defects in a catalyst's crystal lattice may also be produced by the action of heat[328], and the equilibrium concentration of thermal and biographical defects in real crystals may be of the same order as the concentration of active centres[445,446]. Finally, defects may arise and disappear because of chemisorption of the reactant molecules, the chemisorbed species being considered as impurities embedded in the surface of the crystal[328].

Irrespective of their method of production, the defects can move along the surface of the crystal lattice, particularly readily as the temperature is raised, can interact among themselves with their disappearance or the formation of new defects, can be absorbed and generated by the crystal lattice, and, finally, can localise free electrons or holes, thus acting as adsorption centres[328,447-450]. When participating in the chemisorption of the reaction components, the free electrons and holes function as free valences[328]. The free valences are not localised in the lattice, but wander about the crystal, continually arising and disappearing. Their equilibrium concentration in the crystal and on the surface depends on a number of factors, primarily on the nature of the catalyst and the reaction conditions; they may be controlled by external action (illumination, introduction of impurities, etc.). The free valences of the catalyst not only participate in the formation of bonds between the surface and the reactants, but also promote dissociation of adsorbed molecules, with the formation of reactive surface species of radical, ionic, or unsaturated valence type, so that the reactions may proceed by a radical[451] or ionic[328] mechanism. The chemisorbed species may change the nature of their bond with the surface, passing from one state into another. The function of the catalyst is basically to generate these reactive species on the surface by means of the free valences[451,452].

1. P.B.Weisz, C.D.Prater, and K.D.Rittenhouse, J.Chem. Phys., 23, 1965 (1955).
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