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Hydrogenation of Alkenes on Oxide Catalysts

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A qualitative survey of available data has enabled pure oxides to be divided into five groups according to their catalytic activity. Zeolites are less active than oxides corresponding to their cationic forms. The activity of an oxide catalyst either increases continuously or passes through a maximum with increase in its temperature of ignition. This type of dependence is explained by the surface dehydroxylation model on the assumption that the activity is determined by the presence of electron-donating and electron-accepting sites situated side by side on the surface. The hydrogenation of alkenes involves stages of activation of the alkene and of hydrogen, with on most oxides appearance of a semi-hydrogenated form. A list of 91 references is included.

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I. INTRODUCTION

The problem of the hydrogenation of alkenes on oxide catalysts began to attract the attention of research workers only during recent years. Oxides, though less active than metals[1-3], may in several cases have the advantages of being less sensitive to certain catalytic poisons, more highly selective, and easily regenerated. In spite of the large number of experimental investigations, hardly any reviews have appeared covering this field of catalysis. A survey[4] of the conversion of alkenes on oxides contained a short list of references up to 1960.

In the present Review the problem of the hydrogenation of alkenes on oxide catalysts is considered from the points of view of the choice of catalyst, the nature of the catalytic activity, and the kinetics and mechanism of the hydrogenation of alkenes. Factual material is given illustrating the features of reactions on various oxides and on certain multicomponent systems.

II. ACTIVITY OF OXIDE CATALYSTS

1. Individual Oxides

Thirty individual oxides (Table 1) and several mixed oxide systems have been examined as catalysts for the hydrogenation of alkenes. The largest number of investigations have been made on the oxides of zinc, aluminium, and chromium. The alkenes to be hydrogenated ranged from C_2 to C_8, most of the work being done on ethylene and propene.

Tables 2-4 give details of the conditions of preparation of the catalysts and the study of hydrogenating activity. Some 70% of the researches were made by a static method, and the remainder under flow conditions. The temperature range of the investigations was extremely wide, from -120°C for chromic oxide to 500-550°C with alumina, silica, and vanadium sesquioxide. The pressure of the

Table 1. Elements whose oxides have been investigated in the hydrogenation of alkenes.

						H	He	
Li	Be	B	C	N	O	F	Ne	
Na	Mg	Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co Ni
Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh Pd
Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir Pt
Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac	Ku					
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy Ho Er Tm Yb Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf Es Fm Md No Lw

reaction mixture under flow conditions was usually atmospheric, but in the static method it varied from 45 torrs to 60 atm. The molar ratio of hydrogen to alkene usually exceeded unity.

Table 2. Conditions of preparation and activation of oxide catalysts for the hydrogenation of alkenes.

Catalyst	Preparation and activation of catalyst	Alkene	Ref.
MgO	$MgC_2O_4 \xrightarrow[air]{450^\circ} MgO\ (400^\circ, H_2)$	C_2H_4	5
Al_2O_3	$Al(OC_3H_7)_3 \rightarrow Al(OH)_3 \xrightarrow[10^{-5}\ torr]{450-650^\circ} \gamma\text{-}Al_2O_3$	C_2H_4	6,7
	$Al(NO_3)_3 \rightarrow Al(OH)_3 \xrightarrow[air]{650-800^\circ} Al_2O_3$	C_2H_4	8
	$\beta\text{-}Al(OH)_3 \xrightarrow[air]{600^\circ} Al_2O_3\ (500^\circ, H_2)$	C_2H_4	9
	$Al(OR)_3 \rightarrow \beta\text{-}Al(OH)_3 \xrightarrow[10^{-5}\ torr]{600^\circ} Al_2O_3$	C_2H_4	10
	$Al(OC_3H_7)_3 \rightarrow Al(OH)_3 \xrightarrow[vacuum]{650^\circ} Al_2O_3$	C_2H_4	11–13
	$Al(OH)_3 \rightarrow Al_2O_3\ (500^\circ,\ vacuum)$	C_2H_4	14
SiO_2	$Na_2SiO_3 \xrightarrow{HCl} H_2SiO_3 \xrightarrow{800^\circ} SiO_2$	C_2H_4	15
TiO_2	$Ti(C_2O_4)_2 \xrightarrow{NH_4OH} Ti(OH)_4 \xrightarrow[H_2]{670^\circ} TiO_2$	C_2H_4	5
	$Ti(OC_2H_7)_4 \xrightarrow{AcOH} H_2TiO_3 \xrightarrow[air]{670^\circ} TiO_2$ (anatase)	C_2H_4	16
	TiO_2 — rutile (commercial)	C_2H_4	16
V_2O_3	$(NH_4)_3VO_4 \xrightarrow[H_2]{400^\circ} V_2O_3$	C_2H_4	5
	$NH_4VO_3 \xrightarrow{HNO_3} HVO_3 \xrightarrow[H_2]{400^\circ} V_2O_3$	C_2H_4	16
Cr_2O_3	$Cr(NO_3)_3 \xrightarrow{NH_4OH} Cr(OH)_3 \xrightarrow[H_2]{600^\circ} Cr_2O_3$	C_2H_4 C_3H_6 C_6H_{16}	17
	$Cr(NO_3)_3 \xrightarrow{NaOH} Cr(OH)_3 \rightarrow Cr_2O_3$	C_3H_6 C_6H_{16}	18
	$Cr(NO_3)_3 \xrightarrow{NH_4OH} Cr(OH)_3 \xrightarrow[N_2]{500^\circ} Cr_2O_3$	C_2H_4 C_3H_6	19
	$Cr(NO_3)_3 \xrightarrow{NH_4OH} Cr(OH)_3 \xrightarrow[H_2]{450^\circ} \alpha\text{-}Cr_2O_3$	C_2H_4	16
	$Cr(NO_3)_3 \xrightarrow{NH_4OH} Cr(OH)_3 \xrightarrow[vacuum]{425^\circ} Cr_2O_3$	C_2H_4	20
	$Cr(NO_3)_3 \xrightarrow{NH_4OH} Cr(OH)_3 \xrightarrow[H_2]{500^\circ} \alpha\text{-}Cr_2O_3$	C_2H_4	21
MnO	$MnC_2O_4 \xrightarrow[air]{450^\circ} MnO\ (400^\circ, H_2)$	C_2H_4	5
Fe_2O_3	$Fe(NO_3)_3 \xrightarrow{NH_4OH} Fe(OH)_3 \xrightarrow[O_2]{400^\circ} \alpha\text{-}Fe_2O_3$	C_2H_4	16
Co_3O_4	$Co(NO_3)_3 \xrightarrow{NH_4OH} Co(OH)_3 \xrightarrow[air]{450^\circ} Co_3O_4$	C_2H_4	16
NiO	$Ni(OH)_2 \xrightarrow[10^{-5}\ torr]{200^\circ} NiO$	C_2H_4	16
ZnO	$ZnC_2O_4 \xrightarrow[air]{450^\circ} ZnO$	C_2H_4	5
	$Zn(NO_3)_2 \xrightarrow{NH_4OH} Zn(OH)_2 \xrightarrow[H_2]{400^\circ} ZnO\ (260^\circ, vacuum)$	C_2H_4	16
	$ZnC_2O_4 \xrightarrow[vacuum]{450^\circ} ZnO$	C_2H_4	22

Table 2 (Cont'd.)

Catalyst	Preparation and activation of catalyst	Alkene	Ref.
	$ZnCO_3 \xrightarrow{NH_4OH} Zn(OH)_2 \xrightarrow[10^{-5}\ torr]{250^\circ} ZnO$	C_2H_4	23,24
	$ZnCO_3 \xrightarrow{NH_4OH} Zn(OH)_2 \xrightarrow[10^{-5}\ torr]{400^\circ} ZnO$	C_2H_4	25,26
	$ZnO\ (300^\circ, O_2;\ 300^\circ, H_2;\ 450^\circ, vacuum)$	C_2H_4	20
	$ZnC_2O_4 \rightarrow ZnO\ (450^\circ, vacuum)$	C_2H_4	27
	$ZnO\ (300^\circ, H_2;\ 450^\circ, vacuum)$	C_2H_4	28,29
	$ZnO\ (400^\circ, O_2;\ 450^\circ, vacuum)$	C_2H_4	30
	$ZnC_2O_4 \rightarrow Zn(OH)_2 \xrightarrow{400^\circ} ZnO$	C_2H_4	31
	$ZnO\ (500^\circ, vacuum)$	C_2H_4	32
Sc_2O_3	$Sc(OH)(NO_3)_2 \xrightarrow{NH_4OH} Sc(OH)_3 \xrightarrow[10^{-5}\ torr]{600-900^\circ} Sc_2O_3$	C_2H_4	33
Y_2O_3	$Y(NO_3)_3 \xrightarrow{NH_4OH} Y(OH)_3 \xrightarrow[10^{-5}\ torr]{600-900^\circ} Y_2O_3$	C_2H_4	33
	$Y(NO_3)_3 \xrightarrow{NH_4OH} Y(OH)_3 \xrightarrow[air]{650^\circ} Y_2O_3\ (610^\circ, H_2)$	C_2H_4 C_3H_6 C_6H_{12}	34,35
ZrO_2	$Zr(NO_3)_4 \xrightarrow{NH_4OH} Zr(OH)_4 \xrightarrow[10^{-5}\ torr,\ H_2]{600-900^\circ} ZrO_2$	C_2H_4	33
Mo_2O_3	$(NH_4)_2MoO_4 \rightarrow Mo_2O_3$	C_2H_4	5
MoO_{2+s}	$(NH_4)_6Mo_7O_{24} \xrightarrow[2.450^\circ\ vacuum,\ H_2]{1.200^\circ,\ air} MoO_{2+x}$	C_2H_4	36
Ln_2O_3	$Ln(NO_3)_3 \xrightarrow{NH_4OH} Ln(OH)_3 \xrightarrow[air]{650^\circ} Ln_2O_3\ (610^\circ, H_2)$ (Ln=La, Nd, Ho, Er)	C_3H_6	37–39
	$Ln(NO_3)_3 \xrightarrow{NH_4OH} Ln(OH)_3 \xrightarrow[10^{-5}\ torr]{600-900^\circ} Ln_2O_3$ (Ln=La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tu, Yb, Lu)	C_2H_4	33
	$Ln(NO_3)_3 \xrightarrow{NH_4OH} Ln(OH)_3 \xrightarrow[vacuum]{600^\circ} LnO_{2-x} \rightarrow \xrightarrow[H_2,\ 10^{-5}\ torr]{600-900^\circ} Ln_2O_3$ (Ln = Pr, Tb, Er)	C_2H_4	33
$CeO_{2-\delta}$	$Ce(NO_3)_3 \xrightarrow{NH_4OH} Ce(OH)_3 \xrightarrow[H_2,\ vacuum]{600-900^\circ} CeO_{2-\delta}$	C_2H_4	33
HfO_2	$Hf(NO_3)_4 \xrightarrow{NH_4OH} Hf(OH)_4 \xrightarrow[10^{-5}\ torr]{600-900^\circ} HfO_2$	C_2H_4	33
WO_3	WO_3 — commercial (250°, He)	C_2H_4	40

It is evident from Tables 2–4 that quantitative comparison of oxides with respect to catalytic activity is difficult. Besides differences in methods of estimating activity, the oxides differed considerably in mode of preparation and conditions of activation. At the same time a cautious approach is necessary to assessing results obtained in individual investigations. Thus mutually different results were obtained in studies of the catalytic activity of aluminium oxide by six groups of workers [6-14,44]. Analogous differences are observed when a comparison is made of researches on the catalytic activity of the oxides of zinc [5,16,20,22-32] and vanadium [5,16,41]. Germain [45] remarks correctly that "the pretreatment of oxides is so important that some doubt must be cast on the significance of laws

of hydrogenation". Another important factor determining the observed catalytic activity is the purity of the initial alkenes and hydrogen. The poisoning effect of water on the activity of oxides has now been proved. Nevertheless, the degree of purification of the gases was not indicated in the papers cited above. Thus the data in Tables 3 and 4 permit only certain qualitative conclusions on catalytic activities.

Table 3. Activity data on oxide catalysts for the hydrogenation of alkenes, obtained by the static method.

Oxide	Alkene	Reaction conditions: temp., °C	pressure of mixture, torrs	H_2/C_nH_{2n}	Activity* mole $m^2 s^{-1}$ (temp., °C)	Ref.
MgO	C_2H_4	400	760	1.6	0	5
Al_2O_3	C_2H_4	350—450	500	1.0	($\tau_{0.5}$ = 12 min) (450°)	6,7
	C_2H_4	100—200	600	1.0	0	14
SiO_2	C_2H_4	350—500	50—100	1	$6\cdot10^{-11}$ (350°)	15
TiO_2	C_2H_4	400	760	1.2	0	5
	C_2H_4	400	45	2	$1.4\cdot10^{-11}$	16
V_2O_3	C_2H_4	400	760	1	0	5
	C_2H_4	400	45	2	$1.2\cdot10^{-9}$	16
	C_2H_4	400—550	300—600	0.5—2	$1.3\cdot10^{-8}$ (500°)	41
Cr_2O_3	C_2H_4, C_3H_6, C_6H_{12}	350—370	760	1	—	17
	C_2H_4	—120	45	2	$6.3\cdot10^{-8}$	16
	C_2H_4	—78	300	2	—	20
	C_2H_4	0÷40	—	—	—	21
MnO	C_2H_4	400	760	1.5	0	5
	C_2H_4	400	45	2	0	16
Fe_2O_3	C_2H_4	140	75	2	$0.3\cdot10^{-10}$	16
Co_3O_4	C_2H_4	20	45	2	$1.5\cdot10^{-8}$	16
	C_2H_4	—78—30	20—70	1	—	42
NiO	C_2H_4	100	45	2	$2\cdot10^{-9}$	16
	C_2H_4	140	60 (atm)	0.5	—	43
CuO	C_2H_4	180	60 (atm)	0.5	—	43
ZnO	C_2H_4	400	760	1.2	($\tau_{0.05}$ = 60 min)	5
	C_2H_4	100	45	2	$0.9\cdot10^{-8}$	16
	C_2H_4	39—218	600	1.5	$2\cdot10^{-10}$ (56°)	22
	C_2H_4	140—162	50—200	0.5—2	$4\cdot10^{-14}$ (25°)	23, 24
	C_2H_4	80—400	30—300	1	—	25, 26
	C_2H_4	25	300	2	—	20
	C_2H_4	25—60	150	10	$5.5\cdot10^{-9}$ (25°)	27
	C_2H_4	20	130	10	—	28
	C_2H_4	20	130—400	3—10	$5\cdot10^{-9}$	29
	C_2H_4	105—120	100	1	—	31
	C_2H_4	0—30	300	2	—	32
Mo_2O_3	C_2H_4	400	760	1.5	($\tau_{0.01}$ = 60 min)	5
MoO_x	C_2H_4	250	200—700	3	0	36
Sc_2O_3	C_2H_4	—78—20	10	1.2	$0.16\cdot10^{-9}$ (—78°)	33
Y_2O_3	C_2H_4	—78—20	10	1.2	$0.6\ 10^{-9}$(—78°)	33
ZrO_2	C_2H_4	20—400	10	1.2	0	33
Ln_2O_3**	C_2H_4	—78—20	10	1.2	$3.4—0.1\cdot10^{-9}$ (—78°)	33
HfO_2	C_2H_4	—55	10	1.2	$0.06\cdot10^{-9}$	33

* In several cases the activity is expressed as the time τ required to reach a specified degree of conversion.

** Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu.

From the above results it may be supposed that the oxides of titanium, iron, silicon, molybdenum, magnesium, and manganese are almost inactive, while those of aluminium, vanadium, and nickel exhibit slight activity. Cobalt and zinc oxides are moderately active. The most active are chromic oxide, rare-earth metal oxides, and the analogous yttria and scandia, which approach metals in their catalytic properties. Thus chromium and lanthanum sesquioxides are able to catalyse the hydrogenation of ethylene even at −120°C.[33]

A semiquantitative comparison is possible for three groups of oxides. Thus Lazier and Vaughen[5] used a recirculation method to compare the activities of magnesium, titanium(IV), vanadium(III), chromium(III), manganese(II), zinc, and molybdenum(III) oxides. The catalysts differed in method of preparation, but the conditions of activation-treatment with hydrogen at 400°C—were the same (Table 2). Chromic oxide was more active than the zinc and molybdenum oxides; the remaining oxides were inactive. On the whole these results agree with subsequent investigations. Other workers[16] have also found manganese(II) oxide to be inactive. However, varying the conditions of preparation and pretreatment has revealed some slight activity in titanium and vanadium oxides[16,41].

Table 4. Activity data on oxide catalysts for the hydrogenation of alkenes, obtained by the flow method.

Oxide	Alkene	Reaction conditions: temp., °C	pressure of mixture*, abs. atm	H_2/C_nH_{2n}	space velocity, h^{-1}	Conversion, % (reaction rate, mole $m^2 s^{-1}$, at, °C)	Ref.
Al_2O_3	C_2H_4	500	1	5	650	79	8
Al_2O_3	C_2H_4	120—430	0.25	6.5	60 000	(10^{-8}, 200°)	9
Al_2O_3	C_2H_4	200	0.3	8.7	60 000	($1.4\cdot10^{-9}$)	10
Al_2O_3	C_2H_4	—20—240	0.01—0.2	—	—	—	11—13
Cr_2O_3	C_2H_6	200	1	3	200	98	18
	C_6H_{12}	350	—	34	3 400	79	18
ZnO	C_2H_4	0	0.001—0.07	—	60 000	—	30
Y_2O_3	C_2H_4	110	0.5	5	576	100	34, 35
	C_3H_6	185	0.5	3	192	76	34, 35
	C_4H_{12}	320	0.5	—	216	75	34, 35
La_2O_3	C_2H_6	140—210	0.5	3	600—3 000	23—40	37—39
Nd_2O_3	C_2H_6	140—210	0.5	3	600—3 000	49—81	37—39
Ho_2O_3	C_2H_6	140—210	0.5	3	600—3 000	43—72	37—39
Er_2O_3	C_2H_6	140—210	0.5	3	600—3 000	35—59	37—39
WO_3	C_2H_4	125—250	1	5	1 000	($1.6\cdot10^{-7}$, 25°)	40

* Total pressure brought to 1 abs. atm with nitrogen or helium.

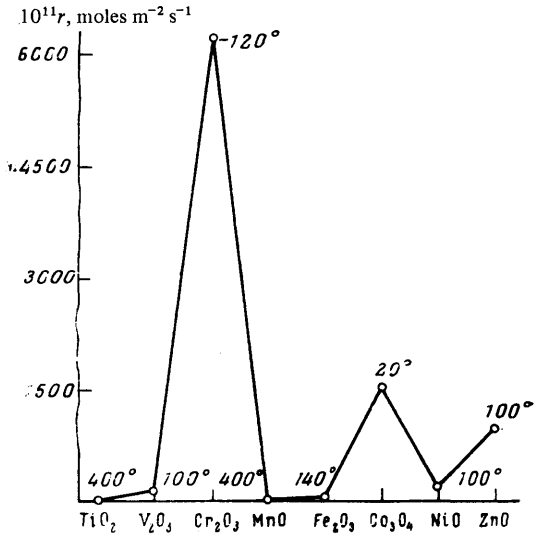


Figure 1. Catalytic activity of oxides of elements in the first transition series towards the hydrogenation of ethylene at various temperatures, where r is the reaction velocity.

Harrison et al.[16] examined the catalytic activity of oxides of transition elements in the fourth period (with the exception of scandium and copper oxides) towards the hydrogenation of ethylene. Comparison of the oxides was not altogether rigorous, for methods of preparation and conditions of activation varied considerably. Furthermore, initial rates of hydrogenation on these oxides were determined at different experimental temperatures. The two-peak pattern of catalytic activity obtained for this series of oxides (Fig. 1) was explained in terms of the electron configuration of the cations containing 3*d* electrons, in conformity with Dowden's ideas[46]. Increase in the coordination number of the cations Cr^{3+} and Co^{3+} from 5 to 6, in contrast to other cations, was accompanied by a greater gain in stabilisation energy of the crystal field. Hence adsorption or other stage accompanied by a change in coordination number was assumed to be the limiting stage. The two-peak pattern of variation in catalytic activity in the series of transition-metal oxides in the fourth period has been confirmed[47] in a study of the hydrogenation of propene by a pulse microcatalytic method.

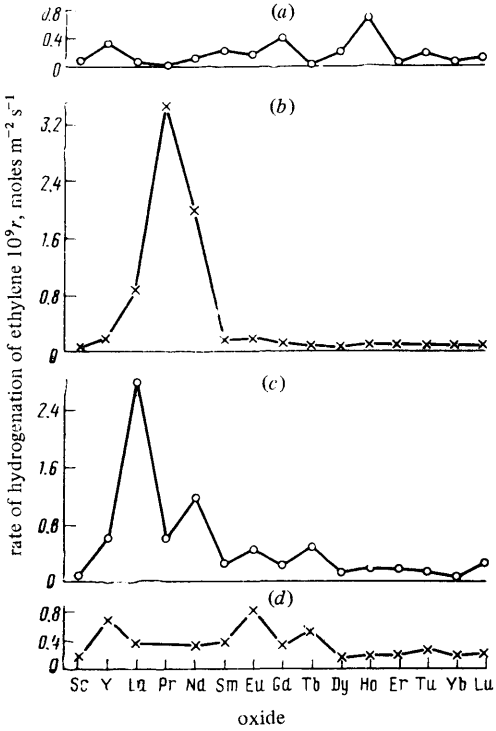


Figure 2. Catalytic activity of rare-earth sesquioxides at different temperatures (after ignition at different temperatures, °C): *a*) 20 (600); *b*) −78 (700); *c*) −78 (800); *d*) −78 (900).

An investigation has been made[33] of the catalytic activity of oxides of rare-earth metals from lanthanum to lutetium, as well as the oxides of scandium, yttrium, zirconium, hafnium, and chromium, towards the hydrogenation of ethylene. All the catalysts were prepared in the same way and were conditioned in a vacuum (to 10^{-5} torr) at various temperatures. Praseodymium, cerium, and terbium oxides were also hydrogenated and the reduced specimens were further conditioned in a vacuum at the same temperature.

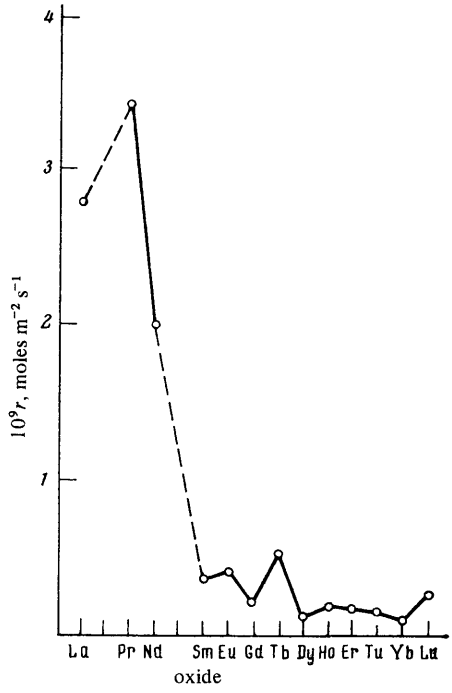


Figure 3. "Maximum" catalytic activity of rare-earth sesquioxides in the hydrogenation of ethylene at −78°C.

The catalytic activity of lanthanum, praseodymium, and neodymium oxides passed through a maximum with increase in the temperature of ignition; with all the other rare-earth sesquioxides the activity increased steadily. This feature of the behaviour of the three oxides was due to their ability to undergo a polymorphic transformation over the temperature range 600–900°C, from a body-centred cubic structure (*C*-form) to a hexagonal structure (*A*-form). It was therefore assumed that the accompanying increase in coordination number of the cation (from 6 to 7) diminished the catalytic activity. A similar conclusion follows also from results for non-stoichiometric oxides of cerium, terbium, and praseodymium. The dioxides of these metals have a fluorite structure with coordination number 8, and do not exhibit catalytic activity. The appearance of activity in the terbium and praseodymium oxides after ignition at 800°C is due to their partial decomposition, leading to a structure, derived from fluorite, with a certain number of vacancies in the oxygen sublattice and some cations having coordination number < 8.

Fig. 2 shows that the law of variation of specific catalytic activity in the series of rare-earth oxides is determined by the temperature of ignition. Thus the activity of lanthanum oxide is least after vacuum treatment at 600°C, and greatest after such treatment at 800°C.

Praseodymium and neodymium oxides exhibit maximum activity after ignition at 700°C, but many other oxides at 900°C. Thus these oxides require different ignition temperatures before they develop their maximum catalytic activity. The results indicate the difficulty of comparing the catalytic activities of oxide systems.

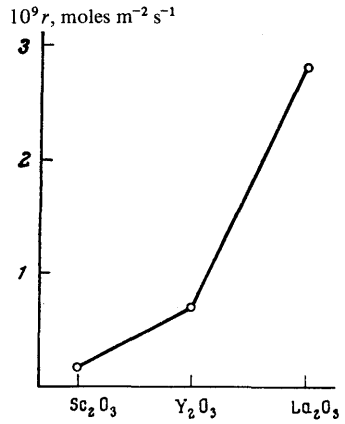


Figure 4. Activity of oxides of the scandium subgroup in the hydrogenation of ethylene at −78°C.

It has been suggested [33] that oxides should be compared after they have been ignited at temperatures ensuring maximum activity. Fig. 3 shows that such comparison gives for rare-earth oxides activities differing by factors of $10-10^2$. In this respect the rare-earth oxides differ significantly from those of transition elements in the fourth period, whose catalytic activities vary by factors of 10^2-10^3. The greatest variation in activity is observed in the series of oxides from lanthanum to gadolinium (cerium subgroup); the remaining oxides (yttrium subgroup) show a less marked variation. It is interesting that the fundamental chemical properties also show greater variation in the former than in the latter subgroup. Scandium and yttrium oxides were closely similar in catalytic activity (Fig. 4), as in many other chemical properties, to oxides of the yttrium subgroup.

Table 5. Hydrogenating activity of oxides (rate of hydrogenation of ethylene at −78°C) and electron configuration of cations.

Oxide	Configuration	$10^9 r$, mole m^{-2} s^{-1}	Oxide	Configuration	$10^9 r$, mole m^{-2} s^{-1}
Sc_2O_3	$3d^0$	0.16	La_2O_3	$4f^0 5d^0$	2.8
TiO_2		0.0 (Refs. 5, 16)	CeO_2		0.0
Y_2O_3	$4d^0$	0.6	Lu_2O_3	$4f^{14} 5d^0$	0.25
ZrO_2		0.0	HfO_2		0.01

Comparison of the activities of a few pairs of oxides (Table 5) indicates that catalytic activity does not depend solely on the electron configuration of the cation. Theoretical views suggested [46] that the activity of scandium oxide would be low, which is inconsistent with recent results [33].

The fall in catalytic activity of the oxides observed from lanthanum to lutetium and from lanthanum to scandium (Figs. 3 and 4) correlates with the decrease in their basicity [48]. This correlation explains also certain other experimental results: (i) acidic oxides—the dioxides of cerium, praseodymium, terbium, zirconium, and titanium—are not active catalysts for the hydrogenation of ethylene; and (ii) acidic impurities—oxides of nitrogen, carbon dioxide, and water—are catalytic poisons.

2. Multicomponent Oxide Catalysts

Study of a chromium–alumina catalyst in the hydrogenation of butene revealed [49] that it was relatively unstable and highly sensitive to traces of moisture, oxygen, and the treatment conditions. The butene was 5–50% hydrogenated over the temperature range 220–340°C. Hydrogenation of ethylene on this type of catalyst [50] gives yields of ethane reaching 80–90% with an equimolecular mixture of ethylene and hydrogen having a space velocity of 1000 h^{-1} at 400–470°C. The hydrogenation of propene on a potassium–chromium–alumina catalyst has been studied [51] by a pulse method at 450–600°C.

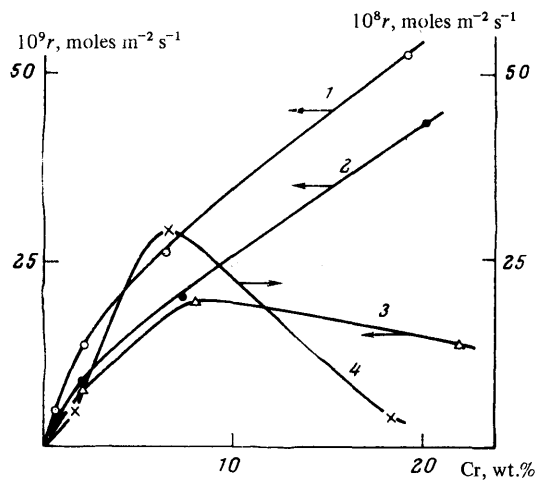


Figure 5. Rate of hydrogenation of ethylene at −78°C on alumina–chrome catalysts obtained by the impregnation with chromium trioxide of: 1) boehmite; 2) bayerite; 3) γ-alumina; 4) hydrargillite.

A circulatory static method, with an equimolecular mixture of hydrogen and ethylene at an initial pressure of 60 torrs, has been used [52] to investigate the effect of method of preparation on the activity of these types of catalyst in the hydrogenation of ethylene at −78°C. The catalysts can be divided into two groups according to the dependence of the activity on the chromium content (Fig. 5). One group includes chromium–alumina catalysts based on boehmite and bayerite (curves *1* and *2*); catalysts prepared from hydrargillite and from γ-alumina belong to the second group. Catalysts of the first group become more active with increase in the chromium content, whereas the activity of the others passes through a maximum at 7–10 wt.% of chromium.

The difference observed between the two types of chromium–alumina catalysts was explained by differences in the distribution of chromic oxide on the carrier surfaces. This involved the postulate that, with boehmite and bayerite catalysts, the proportion of Cr^{3+} ions in the surface layer increased continuously with the concentration of chromic oxide. With catalysts based on hydrargillite and γ-alumina a similar relation is observed only at low concentrations of chromic oxide. With further increase the fine crystals (or clusters) of the oxide become larger, which may lead to a decrease in the surface concentration of Cr^{3+}, and hence in catalytic activity. Catalysts based on hydrargillite are the most active: with 6–8% of chromium their activity is about tenfold that of any other chromium–alumina catalyst, and they are only slightly inferior to chromic oxide, for which the reaction velocity under the same conditions is 50×10^{-8} mole m^{-2} s^{-1}. The introduction of potassium into a boehmite chromium–alumina catalyst diminishes the activity (Table 6).

Table 6.

Potassium, wt.%	0	0.5	1.0	2.0	4.0
$10^9 r$, moles m^{-2} s^{-1}	27	25	23	19	17

Fig. 6 illustrates the degree of conversion of ethylene into ethane on a chromium–alumina catalyst as functions of the partial pressures of water, pyridine, ammonia, and thiophenol. The toxicity of these substances towards catalysts varies in the same sequence as their acidity, which reveals the basic nature of the active centres.

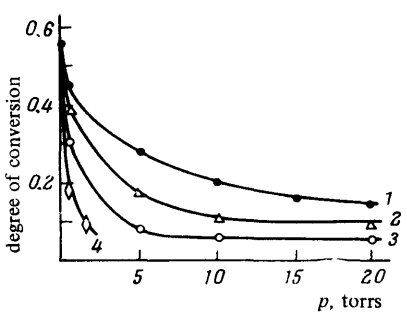


Figure 6. Kinetic isotherms for the poisoning of an alumina–chrome catalyst in the hydrogenation of ethylene at 420°C by: 1) ammonia; 2) pyridine; 3) water; 4) thiophenol.

In the presence of a zinc chromite catalyst[22] ethylene was hydrogenated at 215–250°C. On an $MoO_3.Al_2O_3$ catalyst[53], after activation with hydrogen at 500°C, ethylene was hydrogenated over roughly the same temperature range as on chromic oxide catalysts. A vanadium–aluminium catalyst is active[41] in this hydrogenation at 400–450°C. Komarevsky et al.[54-56] found that this catalyst, reduced with hydrogen at 400°C, catalysed the hydrogenation of butene, hexene, octene, butadiene, and acetylene; under 115 atm at 475°C even benzene could be 27% hydrogenated.

The hydrogenation of heptenes is strongly catalysed by $CoO.MoO_3.Al_2O_3$ over the range 250–275°C.[57] Parravano et al.[58] reported that ethylene can be hydrogenated on an aluminosilicate at 345°C, a result qualitatively confirmed by Topchieva et al.[59] According to these workers aluminosilicates catalyse the hydrogenation of propene only after pretreatment with hydrogen at 550°C. An aluminosilicate containing 0.01% of sodium was more active than a specimen containing a larger quantity. The rate of hydrogenation of ethylene diminishes with increasing acidity of aluminosilicate catalysts[60].

Table 7. Activity (measured by rate of hydrogenation) of neodymium compounds.

Compound	$10^3 r$, mol. s^{-1} Nd^{3+} ion^{-1}
Nd_2O_3, *A*-form	0.15
Nd_2O_3, *C*-form	1.2
74 mole % Nd_2O_3-CeO_2	1.2
37 mole % Nd_2O_3-CeO_2	0
$7Nd_2O_3.9SiO_2$	0.022

Several neodymium compounds have been compared with the *A*- and *C*-forms of the oxide in the hydrogenation of ethylene at −78°C (Table 7).[61] Analysis of the results revealed a relation between the activity and the coordination number of neodymium. The *C*-form of the oxide and a solid solution of 74 mole % of the oxide with cerium dioxide, containing Nd^{3+} in octahedral coordination, had similar activities per cation. The corresponding 37 mole % solid solution was catalytically inactive and contained cations only with coordination number 8. The orthosilicate $7Nd_2O_3.9SiO_2$ contained two types of cations, the relative proportions of which with 7 and 9 coordination were 2 : 5. If it is postulated that the latter cations are inactive, recalculation for cations of coordination number 7 yields a value (8×10^{-5} mol. s^{-1} ion^{-1} Nd^{3+}) very close to the activity of the *A*-form of neodymium sesquioxide with Nd^{3+} ions in the same coordination.

3. Zeolite Catalysts

Until recently few studies had been made of the influence of zeolites on hydrogenations. The activity of γ-type zeolites in the hydrogenation of ethylene was first established by Minachev et al.[62] for the neodymium, calcium, and decationised forms. Hydrogenation took place with a space velocity of 2000 h^{-1} at 78–150°C. With the conditions adopted for regeneration (treatment with air at 500°C for 2 h) the activity of the catalysts diminished from experiment to experiment. The zeolite containing neodymium was more active than the calcium and decationised forms; the sodium form was inactive. It is significant that the hydrogenation of ethylene in the presence of neodymium γ-zeolite was promoted by oxygen, which was later found to activate the hydrogenation of ethylene also with alumina[63].

Results obtained by Topchieva et al.[59,64] using a pulse method indicated that sodium, yttrium, and chromium–zeolites were active in the hydrogenation of propene at

200°C. The activity of the yttrium form depends on the temperature of pretreatment with hydrogen (200–640°C), reaching a maximum after activation at 350°C. Exchange of sodium for yttrium exceeding 50% produces sharply diminished selectivity of hydrogenation. Thus, whereas propane was the only product with yttrium γ-zeolite at a degree of exchange of 46%, the selectivity of the reaction with a specimen having 77% exchange did not exceed 30%. Similar results were obtained with the chromium form (degrees of exchange 4% and 11%). At 200°C the degree of hydrogenation on chromium γ-zeolite reached 23–50%. All specimens rapidly lost their activity. The initial activity of the sodium form was lower than those of the yttrium and chromium forms.

Table 8. Catalytic activity of zeolites and oxides in the hydrogenation of ethylene.

Catalyst	Temperature, °C		Reaction velocity, $10^3 r$, mol. s^{-1} ion^{-1}
	activation	hydrogenation	
0.8CrNaY; Si/Al=2.1	500	—30	3.0
	600	—30	3.1
	700	20	0.5
0.65CrNaY; Si/Al=2.5	450	—40	0.04
	500	—40	0.1
0.27CrNaY; Si/Al=2.5	500	—60	3.4
	600	—60	0.8
0.27FeNaY; Si/Al=2.5	400	400	0.1
	500	400	0.2
0.57LaNaY; Si/Al=2.1	500	20	0.2
0.22NdNaY	500	20	0.8
Cr_2O_3	500	—78	6.6
Nd_2O_3	700	—78	2.0
La_2O_3	800	—78	4.0

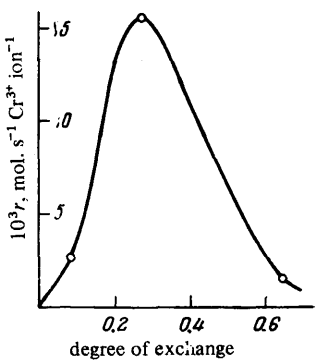


Figure 7. Dependence of activity of CrNa Y-zeolite in the hydrogenation of ethylene at 20°C on the degree of exchange of Na^+ for Cr^{3+}.

A detailed comparative investigation of the catalytic properties of various cation-exchange forms of γ-type zeolites in the hydrogenation of ethylene as functions of the type of cation, degree of exchange, and ratio of silicon to aluminium has been made [65,66] by a circulatory static method with an equimolecular mixture of hydrogen and ethylene at an initial pressure of 60 torrs. This has shown that, after vacuum treatment (10^{-5} torr) over the range 400–700°C (in steps of 100 deg), the sodium, copper, barium, calcium, and decationised forms of the zeolites were inactive from −78 to 400°C. Only zeolites containing tervalent cations—chromium, lanthanum, neodymium, and iron—were active (Table 8). With increase in the fraction of chromium exchange cations from 0.08 to 0.65 the catalytic activity passes through a maximum at a degree of exchange of 0.27 (Fig. 7).

Increasing the ratio of silicon to aluminium from 2.1 to 2.5 (cf. 0.8 CrNa and 0.65 CrNa Y-zeolites [Table 8]) leads to a change in catalytic activity. These results suggest non-uniformity of the active centres, probably due to differences in the distribution of cations among several possible sites [67]. Table 8 indicates also that the chromium form of the zeolite acquires its maximum activity after being heated in a vacuum at 500°C, which was the optimum temperature also for other cationic forms. Ignition at temperatures above 600°C caused irreversible loss of activity, although the zeolites retained their crystalline structure. This peculiarity of behaviour can be attributed to migration [67,68] of cations from large to small cavities, so that ion-exchange cations may form part of the active centres of hydrogenation. This hypothesis is supported by the qualitative analogy between the catalytic properties of oxides and zeolites. Oxides of tervalent elements form the activity sequence

$$Cr_2O_3 > La_2O_3 > Nd_2O_3 \gg Fe_2O_3,$$

which on the whole is consistent with that of the zeolites

$$CrNaU > NdNaU > LaNaU \gg FeNaU.$$

The activation energies for the hydrogenation of ethylene on oxides and zeolites are roughly equal at 3–6 kcal $mole^{-1}$. The lower activity of zeolites than of oxides may evidently be attributed to steric inaccessibility of some of the ion-exchange cations.

Table 9.

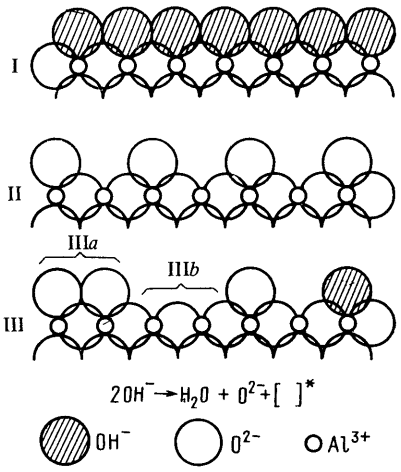
Zeolite	NaM	LiM	KM	CaM	MgM	ZnM	CdM	HM
Cyclohexane, %	98.3	87.7	11.0	98.6	69.4	59.7	17.4	19.7

Cationic forms of mordenite were first shown by Minachev et al. [69–71] to catalyse the hydrogenation of ethylene and benzene. Under the conditions adopted—$4H_2 + C_2H_4$ with space velocity 750 h^{-1} under 1–30 atm at 215–235°C—ethylene was completely hydrogenated in the presence of NaM zeolite; with the potassium form hydrogenation was 20–92% complete. Table 9 gives the yields of cyclohexane from the hydrogenation of benzene (C_6H_6 + $5H_2$ at 1 h^{-1} under 30 atm at 250°C).

III. NATURE OF THE CATALYTIC ACTIVITY

Despite the differences in approach by different authors and the use of an extremely wide range of methods, only a limited number of hypotheses have been made on the nature of the catalytic activity: (i) many workers suppose that coordinatively unsaturated cations are present in the active centre; (ii) in several papers catalytic activity was associated with ions of metals in a certain valency state; and (iii) several investigators assume that an active centre contains not only cations but also oxygen ions.

The first hypothesis provided an explanation for the many experimental data on the influence of heat-treatment conditions and the reversible poisoning effect of water vapour on the catalytic activity of oxides of aluminium [6,7], zinc [24,25,28,29], chromium [16-20], rare-earth metals [33-35], and silicon [15], as well as that of zeolites [66]. On this hypothesis the reason why oxides must be ignited for catalytic activity to develop is that, under the usual conditions of storage, the surface becomes hydrated by contact with atmospheric moisture, and contains no coordinatively unsaturated ions. The increase in activity as the temperature of ignition of the oxides is raised is attributed to increase in the number of such cations. The activity of zeolites passes through a maximum as this temperature is raised, which could be explained [66] by two factors: the activity of the zeolites is increased by the appearance of coordinatively unsaturated cations at high temperatures; on the other hand, the number of cations accessible to reactant molecules diminishes because of their migration into small cavities. Incorporation of cations into active centres follows also from the identity of the activity sequences of oxides and corresponding cationic forms of zeolites.



* Anionic vacancy on surface.

Figure 8. Diagram of cross-section through surface of aluminium oxide at various stages of dehydroxylation, with the surface: I) completely hydrated; II) completely dehydroxylated; III) partly dehydroxylated.

However, no quantitative comparison between the number of cations in a certain coordination environment and catalytic activity was made in the above studies. Such comparison is now possible for alumina, whose ability to catalyse the hydrogenation of ethylene at 250–450°C appears only after heat-treatment at 450°C, [6,7] when at least 30% of the surface aluminium ions change their coordination from 6 to 5. [72] Yet according to Weller and Hindin [7] the number of active centres does not exceed 1–2% of the total number of surface ions, since at this particular coverage with water the catalytic activity of alumina is completely lost. Raising the temperature of ignition from 450 to 550°C increases the number of coordinatively unsaturated cations only by 30%, while the catalytic activity increases by a factor of 20! Thus no direct functional dependence is present between the total number of coordinatively unsaturated cations and catalytic activity.

This conclusion suggests the non-uniformity of such cations, which is clearly illustrated by Peri's model of dehydroxylated aluminium oxide [72]. The partly dehydroxylated surface (Fig. 8) contains a disordered layer of ions: at some sites (III*a*) oxygen ions accumulate in direct contact, and at others (III*b*) coordinatively unsaturated cations are situated side by side. Catalytic activity towards hydrogenation could then probably be related to sites of the latter type. Their ability to catalyse migration of the double bond in butenes had earlier been proved by Peri [73]. The number of such sites (Fig. 8—II and III) and hence also the catalytic activity of the oxide should pass through maxima with increase in the degree of dehydroxylation (and in the ignition temperature). This conclusion is consistent with results for chromic oxide [33] and zinc oxide [23].

The relation between catalytic activity and the valency state of the cations has been discussed. Chromic oxide, CrNa Y-zeolite, and chromium–alumina catalysts strongly catalysed the hydrogenation of ethylene in the absence of Cr^{2+} ions [74]. Catalysts containing a considerable quantity of Cr^{5+} and Cr^{6+} ions were inactive, which allows us to reveal the catalytic activity of Cr^{3+} ions. With cerium, praseodymium, and terbium the sesquioxides also possessed catalytic activity, but the dioxides were almost inactive. Under the experimental conditions [74] ions of bivalent rare-earth metals were not formed, and hence the activity of these elements was due to the tervalent cation.

It was postulated in most of the above papers that ethylene underwent hydrogenation on a centre containing not only a cation but also an oxygen ion, but no evidence was given. Such evidence includes [33] the relation found between catalytic activity and basicity, which may be governed [75] by the oxygen ions.

IV. KINETICS AND MECHANISM OF THE HYDROGENATION OF ALKENES

The mechanism of the hydrogenation of alkenes (mainly ethylene) has been studied most thoroughly on the oxides of aluminium, zinc, chromium, and rare-earth metals. Kinetics, infrared spectroscopy, thermal desorption, and other methods enabling the reactivity of adsorbed species to be estimated have been used. In a few cases a tracer technique was applied. Since a kinetic method has been used most frequently, we begin with an account of the principal results obtained in studies of the kinetics of hydrogenation.

Table 10 shows that many kinetic equations have been suggested. One example indicated that the reaction velocity is almost independent of the partial pressures of the components [22]. According to others [23-26,35,38,39,77] the rate is determined solely by the pressure of hydrogen or ethylene. Two formulae [41,39] were of the first order with respect to the initial reactants, and in three cases [9,48,53] equations of the type $r = kP_{H_2}P_{C_nH_{2n}}^{0.5}$ were found. Thus inspection of Table 10 indicates that the kinetic orders with respect to hydrogen and the alkene usually vary from first to zero. The rate of the reaction is unaffected by the pressure of alkanes, except in experiments with silica and $CoO.MoO_3.Al_2O_3$ catalysts. The form of the kinetic

equation depends on the chemical composition of the specimen, the conditions of pretreatment, and the temperature range of the investigation (cf. *2* and *3*, *9–11*, *13* and *14* in Table 10). The activation energy of the reaction varies over a wide range, from 0 to 24 kcal mole^{-1}, probably being a function of temperature. With the oxides of aluminium, zinc, and rare-earth metals the activation energy falls to zero with rise in temperature.

Table 10. Kinetic equations and activation energies of hydrogenation of alkenes on oxides.

No.	Catalyst	Equation	Activation energy, kcal mole^{-1}	Temp. range, °C	Ref.
1	Al_2O_3	$r = kP_{H_2}P^{0.5}_{C_2H_4}$	9 0	120—180 300—430	9
2	Al_2O_3	$r = kP_{H_2}(1-\theta_{C_2H_4})\,\theta_{C_2H_4}$	7.7	−20—+25	11 *
3	Al_2O_3	$r = kP_{H_2}\,\theta_{C_2H_4}$	0	90—240	11
4	SiO_2	$r = kP_{H_2}/(1+K'P_{C_2H_4})$	8	350—500	15
5	V_2O_3	$r = kP_{H_2}P_{C_2H_4}$	22.0	400—550	41
6	Cr_2O_3	$r = kP^{1.5}_{H_2}P^{1.5}_{C_2H_4}$	18	200—350	18
7	ZnO	$r = kP^{0.1}_{C_2H_4}$	18	39—56	22
8	ZnO	$r = kP_{H_2}$	22	140—162	23, 24
9	ZnO	$r = kP_{H_2}$	22	80—125	25, 26
10	ZnO	$r = kP^{0.3}_{H_2}P^{0.7}_{C_2H_4}$	4.5	140—175	25, 26
11	ZnO	$r = kP_{C_2H_4}$	0	210—225	25, 26
12	ZnO	$r = kP^{0.5}_{H_2}\cdot\theta_{C_2H_4}$	—	20	29 *, 76
13	M_2O_3 (Y, La, Ho, Er)	$r = kP^{0.5}_{H_2}$	5—6	130—180	35, 38, 39
14	M_2O_3 (Y, La, Ho, Er)	$r = kP_{H_2}P_{C_2H_4}$	0	230—260	35, 38, 39
15	WO_3	$r = kP_{H_2}P^{0-1}_{C_2H_4}$	—	125—250	40
16	$V_2O_3\cdot Al_2O_3$	$r = k[a+(K_pH_2)^{0.5}]P_{C_2H_4}$	7.6	400—550	41
17	$Cr_2O_3\cdot Al_2O_3$	$r = kP_{H_2}P^{0.5}_{C_2H_4}$	10	220—340	48
18	$MoO_3\cdot Al_2O_3$	$r = kP_{H_2}P^{0.5}_{C_2H_4}$	4	150—450	53
19	$CoO\cdot MoO_3\cdot Al_2O_3$	$r = kP_{H_2}(P_{C_nH_{2n}}/P_{C_nH_{2n+2}})$	22.5—24.5	250—375	57
20	Y_2O_3, La_2O_3, Ho_2O_3	$r = kP_{H_2}$	5—6	−22—−22	77

* Experiments conducted in a stream of hydrogen after preliminary adsorption of ethylene, where θC_2H_4 is the degree of surface coverage with ethylene.

The kinetic results can equally well be explained by the ideas of Eley and Rideal, who assume activation of only one of the reactants (hydrogen or alkene), and by those of Langmuir and Hinshelwood, who regard the interaction of adsorbed species as the limiting stage. In most of the papers cited it is assumed that the catalytically active surface is homogeneous. Nevertheless, the kinetic equations with fractional powers of reactant partial pressures (Table 10) can be explained also by energetic non-uniformity of the active centres.

Sinfelt [9] explained the kinetics of the hydrogenation of ethylene on aluminium oxide by means of Twigg's mechanism [78], involving a stage of interaction between hydrogen adsorbed by van der Waals forces and chemisorbed ethylene:

$$C_2H_4 \underset{2}{\overset{1}{\rightleftarrows}} \underset{*}{CH_2}—\underset{*}{CH_2},$$

$$\underset{*}{CH_2}—\underset{*}{CH_2} + H_2 \overset{3}{\underset{6}{\rightleftarrows}} \underset{*}{\overset{CH_3}{CH_2}} + H \overset{5}{\rightarrow} C_2H_6 .$$

A comparative study of the catalytic activity of aluminium oxide towards the hydrogenation of ethylene and of hydrogen–deuterium exchange data suggested [6,7] that activation of ethylene was the limiting stage. Lucchesi et al. [79] detected by infrared spectroscopy the adsorbed ethylene and ethyl assumed in Twigg's mechanism.

Amenomiya and Cvetanovic [80] used thermal desorption to examine the mechanism of the hydrogenation of ethylene on aluminium oxide, and established the presence of two types of adsorption centres, differing in energy of bonding with ethylene. These centres occupy 2.8% of the alumina surface; 60% of them have an activation energy of desorption of 26.8 kcal mole^{-1}, and 40% an activation energy of 36.4 kcal mole^{-1}. Hydrogenation of ethylene occurred more readily on centres of weak adsorption. Ethylene sorbed on them gave with deuterium 1,2-dideuteroethane, which was regarded as indicating hydrogenation by Twigg's scheme. Interaction of the firmly bound ethylene with deuterium gave a mixture of all possible deuteroethanes, which was explained by a mechanism analogous to that suggested by Horiuti and Polanyi [81]:

$$\left.\begin{array}{l} C_2H_4 \rightleftarrows C_2H_{4\,ads} \\ H_2 \rightleftarrows \begin{cases} H_{ads} \\ H_{ads} \end{cases} \end{array}\right\} \rightleftarrows C_2H_{5\,ads} \Big\} \rightarrow C_2H_6 \Big\} .$$

This involves a stage of dissociative chemisorption of hydrogen on centres with weak bonding of ethylene, and the formation of ethane via a semi-hydrogenated state.

An attempt [7] at a geometrical interpretation of the activation of ethylene on aluminium oxide suggested two possible mechanisms—adsorption of ethylene on two neighbouring aluminium ions in the corundum structure or two-point adsorption on an aluminium ion and an oxygen ion—the length of the aluminium–carbon bond being taken as 1.8 Å in both cases (as in aluminium alkyls). The activation of ethylene on vanadium sesquioxide was assumed [18] to involve adsorption on two vanadium cations.

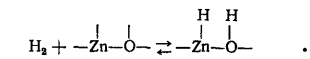
Interesting results were obtained in studies of the mechanism of the hydrogenation of ethylene and propene on chromic oxide, which showed [19,20] that hydrogenation with deuterium at −78°C did not involve exchange with the hydrogen of the hydrocarbons. The hydrogenation of ethylene with an equimolecular mixture of gaseous hydrogen and deuterium gave [20] ethane, deuteroethane, and dideuteroethanes. Conner and Kokes [20] therefore assume dissociative chemisorption of hydrogen and successive addition of hydrogen atoms. A similar conclusion concerning the mechanism of the hydrogenation of ethylene on cobalt oxide between −78 and 30°C was drawn by some Japanese workers [42] from a study of reaction velocities and product compositions for the four systems

1. $C_2H_4 + H_2$
2. $C_2H_4 + D_2$
3. $C_2H_4 + C_2D_4 + H_2$
4. $C_2H_4 + H_2 + D_2$.

The largest number of investigations on the mechanism of hydrogenation have been made with zinc oxide. Teichner et al. [23-26,82], on the basis of a kinetic study, suggested a mechanism involving interaction between associatively adsorbed ethylene and dissociatively sorbed hydrogen. In contrast to the Horiuti–Polanyi scheme [81], all stages were assumed to be in equilibrium. This scheme was made somewhat more detailed. Catalytic

activity was found[23,24] to be independent of the concentration of electrons in the conduction band. This was regarded as indicating a covalent form of chemisorption of hydrogen, as was confirmed also by infrared spectroscopy.

On the basis of infrared spectra Dent and Kokes[28] consider that hydrogen is chemisorbed on coordinatively unsaturated zinc and oxygen ions:



An analogous conclusion was reached by Eischens et al.[83] In the view of the former workers[84] the chemisorption of ethylene is a consequence of π-electron interaction with oxygen ions. Hydrogenation of adsorbed ethylene takes place by the successive addition of hydrogen atoms bound to zinc and oxygen atoms. In the first stage π-adsorbed ethylene becomes detached from oxygen and bound in its semi-hydrogenated form to a zinc atom. The truth of this mechanism is confirmed[85] by the detection, in the infrared spectra, of the compound $Zn-C_2H_5$, which on treatment with hydrogen disappeared at a rate closely similar to the rate of hydrogenation. Krause[86] also supposes that the hydrogenation of ethylene on zinc oxide involves an intermediate semi-hydrogenated form adsorbed on zinc atoms. In contrast to Dent and Kokes[28,84], he assumes that the π-adsorbed ethylene is attached only to zinc atoms.

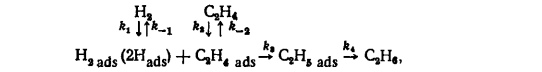
Table 11. Results for the mechanism of the hydrogenation of ethylene on dysprosium sesquioxide at −55°C.

No.	Initial compound	Reaction products
1	$OH_{surf} + D_2$	HD found only at ⩾ 120°C
2	H_{ads} (w + s)*** + D_2	HD in minor quantity
3	H_{ads}(s) + D_2	HD not detected
4	H_{ads}(w + s) + C_2D_4	$C_2H_2D_4$ not detected
5	$C_2D_{4,ads} + H_2$	$C_2H_2D_4$
6	$C_2H_4 + H_2$	C_2H_6; $r = 0.46 \times 10^{-9}$*
7	$C_2H_4 + D_2$	99% $C_2H_4D_2$; $r = 0.30 \times 10^{-9}$
8	$C_2D_4 + H_2$	97% $C_2D_4H_2$; $r = 0.42 \times 10^{-9}$
9	$C_2H_4 + C_2D_4$	HD, $C_2H_{4-x}D_x$, $C_2H_{6-x}D_x$— not detected
10	$C_2H_6 + D_2$	HD, $C_2H_{6-x}D_x$—not detected
11	$H_2 + D_2$	HD, $r = 0.38 \times 10^{-9}$
12	$C_2H_4 + H_2 + D_2$ (1.7:1:1)	47% C_2H_6, 21% C_2H_5D, 32% $C_2H_4D_2$; HD**

* Rates of reaction for 50% conversion r, mole m^{-2} s^{-1}.
** Detected only after ethylene had been completely hydrogenated.
*** Weakly (w) and strongly (s) adsorbed.

Baranski and Cvetanovic[30] have been able by means of thermal desorption to study the reactivity of five forms of adsorbed hydrogen and two forms of ethylene. They found that only the most weakly bound forms of hydrogen and ethylene take part in hydrogenation. The heat of adsorption of such ethylene is 4–6 kcal $mole^{-1}$. The yellow colour of tungsten oxide does not vanish when ethylene undergoes hydrogenation on the oxide. This suggested[40] that the reaction does not involve atomic hydrogen, and that ethane is formed by Twigg's scheme of interaction of physically adsorbed hydrogen with chemisorbed ethylene.

The mechanism of the hydrogenation of ethylene and propene on rare-earth oxides has been studied by both kinetic and isotope methods. Kinetic investigations by Topchieva et al.[35,38,39] established for the temperature range 130–190°C a mechanism of hydrogenation analogous to that of Polanyi and Horiuti[81], with interaction between the adsorbed alkene and dissociatively chemisorbed hydrogen assumed to be the limiting stage. The mechanism of the low-temperature hydrogenation of ethylene on dysprosium sesquioxide has been examined by isotope and thermal-desorption methods[33,87-89]. A series of reactions which might hypothetically occur in the ethylene–hydrogen–oxide system was studied (Table 11). It is evident for reaction *1* that the hydrogen of surface hydroxyls is not exchanged, and is probably not involved in hydrogenation, under the conditions of catalysis (−55°C). In conformity with reactions *2* and *3* it was established that the two different forms of chemisorbed hydrogen differed in reactivity. These results suggested that firmly sorbed hydrogen played no part in hydrogenation. Reactivity of adsorbed ethylene was shown in reaction *5*. The hydrogenation of ethylene (reactions *7* and *8*) gave only simple addition products. These results indicate absence of dissociative adsorption of ethylene or the ethane formed, which is supported by the investigation of reactions *9* and *10*, when the hydrogen of the hydrocarbons (ethane and ethylene) is not exchanged. Yet in the hydrogenation of ethylene with a mixture of protium and deuterium (reaction *12*) the products of simple addition—ethane and dideuteroethane—were accompanied by deuteroethane C_2H_5D, although H_2-D_2 exchange does not take place under the conditions of hydrogenation. Thus the above investigation shows that the reaction may occur via a semi-hydrogenated form:



where stage 3 is irreversible.

Comparison of rates of hydrogenation of ethylene by reactions *6* and *7* revealed a kinetic isotope effect $r_H/r_D = 1.5$. Yet rates of hydrogenation of deuteriated and ordinary ethylene (reactions *6* and *8*) were almost the same. Hydrogen–deuterium exchange and the hydrogenation of ethylene took place at closely similar rates. Furthermore, the activation energies of the two reactions are also equal at ~ 5 kcal $mole^{-1}$. These results suggest that the hydrogenation of ethylene is limited by the activation of hydrogen. Nevertheless, such an assumption does not mean that hydrogenation can take place e.g. by the interaction of chemisorbed hydrogen with physically sorbed ethylene, according to Jenkins and Rideal's mechanism[90]. In the presence of oxide catalysts migration of the double bond in butenes is considerably more rapid than hydrogenation[66,91]. The sequences of catalytic activity of oxides for these reactions were closely similar, which suggested that active centres for activation of the double bond and for hydrogenation were analogous in nature. The mechanism of catalytic hydrogenation should therefore involve both stages—chemisorption of the alkene and chemisorption of hydrogen.

V. CONCLUSION

The information reviewed above shows that oxide catalysts are more complicated than metallic catalysts[1-4]. Work on the latter has developed several methods for obtaining pure and crystallographically uniform surfaces,

which has permitted the comparison of metals according to their specific catalytic activity. With oxide catalysts such comparison encounters several difficulties, primarily because of the significant dependence of catalytic activity on conditions of pretreatment. This dependence is not always due solely to the desorption of impurities, as with metals, but is connected with surface oxidation, reduction, and dehydroxylation. Changes in chemical composition are often accompanied by crystallographic changes, which may also influence catalytic activity. This was shown quite clearly by the catalytic properties of oxides of rare-earth metals.

Existing data indicate that, with rise in the temperature of ignition, the activity of an oxide catalyst per square metre of surface increases to a certain limit or else passes through a maximum. The present Reviewers have therefore proposed comparing the "maximum" activities of oxides. However, the effect of ignition temperature on the activity of several oxides has not been studied, so that this approach does not lead to a quantitative comparison of all the catalysts studied.

Qualitative consideration of the data enables oxides to be divided into four groups

(1) very active—Cr_2O_3, La_2O_3, Pr_2O_3, Nd_2O_3

(2) active—Sc_2O_3, Y_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tu_2O_3, Yb_2O_3, Lu_2O_3

(3) moderately active—Co_3O_4, ZnO

(4) relatively inactive—V_2O_3, NiO, Fe_2O_3, Al_2O_3, SiO_2, HfO_2.

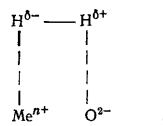
The oxides—ZrO_2, MoO_{2-x}, MgO, MnO, TiO_2, CeO_2, Pr_6O_{11}, and Tb_4O_7—exhibit hardly any activity.

It follows from the above enumeration that hitherto no study at all of catalytic activity has been made on the oxides of gallium, indium, thallium, germanium, tin, lead, niobium, tantalum, antimony, bismuth, tellurium, alkali metals, transuranium elements, and certain other elements intermediate in properties between metals and non-metals. No data are available on the catalytic properties of oxides of the platinum subgroup.

The lack of data for many oxides and the limited study made of others are probably among the main factors preventing any general approaches to the prediction of catalytic activity. The ideas of Dowden, who discussed the energetics of the interaction of an adsorbed particle with a coordinatively unsaturated cation, provide a partial understanding of the variation of activity in oxides of the first transition series. In order to explain the catalytic properties of rare-earth oxides the Reviewers suggested that activities were determined by interaction of an adsorbed molecule with a basic centre. This hypothesis provided a qualitative explanation also of the decrease in activity on passing from oxides to zeolites and silicates.

Thus the development of approaches to the forecasting of catalytic action depends on elucidation of the chemical nature and the structure of the active centre. However, an exact solution of the problem is impossible without elucidation of the chemical nature of the adsorbed species interacting on the surface and the mechanism of the reaction. Despite the abundance of kinetic papers, the mechanism of hydrogenation remains little studied. In experiments with butenes not only can hydrogenation be followed but the main laws governing migration of the double bond, which requires activation of the latter, can be determined. A series of oxides shows analogous variation in activity towards hydrogenation and towards migration of the double bond, which suggests that the active centres for activation of the alkene and for its hydrogenation are the same in nature. Migration of the double bond always occurs under milder conditions and at higher rates than does hydrogenation, which leads to the postulate that activation of hydrogen is the limiting stage. This conclusion has been proved experimentally in a study of the mechanism of the hydrogenation of ethylene on dysprosium oxide.

In spite of the differences in systems studied and in methods of investigation, most workers now consider that the active centre contains an ion-pair comprising a coordinatively unsaturated cation and an oxygen ion, which adsorb a polarised hydrogen molecule:



This mechanism of activation of the hydrogen molecule suggests that a correlation will exist between catalytic activity and the polarising effect of the ion-pair, which on the whole is apparent. Published information indicates that oxides of trebly charged cations are the most active, whereas those containing doubly and quadruply charged cations either are relatively inactive or do not catalyse hydrogenation at all. It follows also from the above mechanism that easily polarisable substances will act as poisons of catalytic hydrogenation. The relation found between the toxicity of poisons and their ability to abstract a proton supports the hypothesis that catalytic activity is due to an ion-pair. Metals, on the other hand, are not poisoned by most of the substances that are highly toxic to oxides (e.g. water, pyridine, alcohols, ketones).

In the case of alumina, detailed investigation has shown that not all coordinatively unsaturated ions are catalytically active. Centres of catalytic activity may be two adjacent segments of the surface (electron-donating and electron-accepting), respectively aggregates of coordinatively unsaturated cations and of oxygen ions. The diminished catalytic activity of oxides after ignition at high temperatures can be explained in terms of such a model by a redistribution of surface oxygen ions leading to a regular surface structure.

The absence of sufficiently accurate models of the surface for most oxides is currently a serious obstacle to confirming or refining existing views on the nature of active centres.

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