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Catalytic Properties of Rhenium and Its Compounds

M.A.Ryashentseva and Kh.M.Minachev

The most promising applications of rhenium are in electronics, radio technology, electrical technology, and the vacuum electronics industry. The present review deals with the application of rhenium and its compounds as catalysts for various reactions in organic synthesis. 107 references.

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I. INTRODUCTION

Since its discovery in 1925, rhenium has claimed a special place among the rare elements[1,2]. Its existence was predicted by Mendeleev, who called the element dvi-manganese. Rhenium belongs to Group VII of the Periodic Table, with atomic number 75, atomic weight 186.3, atomic radius 1.361 Å, and a hexagonal lattice with lattice parameters $a = 2.765$ Å, $c = 4.470$ Å, $c/a = 1.61$. Its melting point (3170°) is the third highest after diamond and tungsten, and its physical properties are similar to those of the refractory metals of Group VI. Due to the presence of five electrons in the 4*d* shell, which are available for covalent bond formation in addition to the two 6*s* electrons, rhenium is a fairly reactive element. The chemical properties of rhenium are similar to those of the Group VII metals (in particular, manganese). The metal is stable towards oxidation and shows remarkable corrosion resistance in moist and aggressive ambients. The most stable oxygen, sulphur, and selenium compounds of rhenium are those in which the element has a valence of four or seven (ReX_2 and Re_2X_7, where X = O, S, Se). Several reviews of the chemistry of rhenium and its compounds have appeared[3-19].

Rhenium is used at present as an electrical contact material, for metallic coatings, for alloys having special physical properties, as an additive in corrosion-resistant alloys, etc. The demand for rhenium and rhenium salts is increasing continuously in the USSR as well as in the USA, Germany, Britain, and France.

The production of rhenium in the USA had reached 1000 tons per annum in 1957[17], the main deposits of rhenium being found in that country. In countries where platinum resources are inadequate, the search for alternative catalysts is an urgent problem: rhenium offers attractive possibilities in this direction. The fact that rhenium lies close to the platinum group metals in the Periodic Table suggests comparable catalytic properties in the presence of hydrogen: in particular, the ability to catalyse hydrogenation and dehydrogenation reactions, activation of unsaturated bonds, promoting action, etc. The properties of rhenium supported on various carriers are being extensively studied. When producing a catalytically active surface it is important to choose a metal which will not suffer recrystallisation during the catalytic reaction. Hence, metals with a high melting point and resistant to ageing effects are particularly valuable. Rhenium is very promising in this respect because of its high melting point and its closely packed structure.

No systematic investigation of the catalytic properties of rhenium was published until the 1930's, the only information being found in the Patent literature. The recent discovery of the element, and the high cost of its production, may have been responsible for the lack of open publications.

Thus, the use of rhenium as a catalyst for the chlorination of methane to chloroform, and of rhenium sulphide on active carbon for the dehydrogenation of fuel oils under pressure and for the synthesis of ammonia, is disclosed in a number of Patents[20-28]. Deuterium can be obtained from D_2O by exchange with hydrogen in the presence of Re_2S_7. Rhenium oxide and rhenium salts have been proposed for the oxidation of sulphur dioxide to sulphur trioxide; colloidal rhenium (in large excess) has been used for the reduction of the double bonds in maleic and cinnamic acid. Fast isotope exchange between water and deuterium has been reported on a rhenium heptasulphide catalyst supported on carbon[29]. The replacement of deuterium by hydrogen in heavy water occurs also in the presence of metallic rhenium[30,31]. Rhenium is not normally used as an oxidation catalyst because its oxides are too volatile in an oxidising medium[32]. However, telluric oxide containing 5% of rhenium oxide[33] is used for the selective oxidation of methyl or methylene groups adjacent to a double or a triple bond by a phenyl radical or hydroxyl group. In the oxidation of propene by air to acrolein[34,35], the yield is ~16% on a catalyst containing rhenium oxide as compared with ~2% on a catalyst without rhenium oxide. Alloy catalysts have a high activity in the vapour-phase oxidation of sulphur dioxide to sulphur trioxide[36,37]. Small additions of rhenium to these catalysts increase their catalytic activity and improve their stability towards poisoning. Thus, tungsten is relatively inactive towards the oxidation of sulphur dioxide to sulphur trioxide, but it becomes active when alloyed with 10% of rhenium. In the presence of this alloy, supported on glass wool, the extent of reaction is 75%, whereas it is only 30% when the rhenium is omitted. In the oxidation of ammonia[34,35] a platinum–rhenium alloy gives a higher yield of product than does the simple platinum catalyst as

well as showing higher uniformity and resistance to poisoning. In aqueous solutions[33] rhenium oxide can be used for the oxidation of nitrites to nitrates and sulphites to sulphates.

Tropsch and Kassler[38,39], who studied the hydrogenation of ethylene to ethane and the production of methane from CO_2 and H_2, and demonstrated the large increase in activity resulting from the addition of rhenium to a copper catalyst, also published their work in the 1930's. These authors suggested the possibility of hydrogenating unsaturated hydrocarbons containing not less than three carbon atoms. Schmidt[40] pointed out that rhenium is inferior to platinum, palladium, and nickel in dehydrogenating power.

Evidently, only fragmentary knowledge of the catalytic properties of rhenium was available in the 1930's. During the 1940's, and particularly since 1960, intensive studies of the catalytic properties of rhenium began, both in the Soviet Union and abroad, concurrently with the greater availability of the element.

II. RHENIUM AND ITS OXYGEN, SULPHUR, AND SELENIUM COMPOUNDS (dehydrogenation of alcohols and reduction of various organic compounds)

Platonov and coworkers[41-49] showed that finely divided rhenium at room temperature is relatively inactive towards the hydrogenation of maleic acid and cyclohexene. On raising the temperature to 250° the element catalyses the hydrogenation of benzene, cyclohexene, nitrobenzene, and nitric oxide. Up to 22% of cyclohexane is formed from cyclohexene[41]. A simple method of preparing rhenium in a disperse and active form from ammonium perrhenate — the "nitric acid" method — has been described[41]. Acetone was obtained in 85% yield by dehydrogenation of isopropanol on a finely divided rhenium catalyst[42,43] at 400°; from n-propanol, propionaldehyde was obtained in 20.8% yield. Isopropanol is dehydrogenated much more readily than n-propanol on a rhenium catalyst[43], but not so readily as n-butanol[44]. The dehydrogenation of isopentanol has also been investigated[45]: no side-products (acids, esters, unsaturated compounds) are found in the catalysis product. Cyclohexanol at 450° gives[47] up to 25% of cyclohexanone, and small amounts of cyclohexene, benzene, and a trace of phenol. Known alcohol dehydrogenation catalysts, such as platinum, nickel, zinc, and copper, were shown to have a lower activity and selectivity.

The dehydrogenation properties of rhenium catalysts have been studied[45] by examining the decomposition of formic acid ($HCOOH \rightarrow CO_2 + H_2$). The activity of the rhenium catalyst was found to be comparable to (or higher than) the activity of spongy Pt, Pd, and Cu catalysts. The percentage decomposition to CO_2 and H_2 was 8.7, 57.5, 100, and 100% at 100, 175, 230, and 250° respectively.

Broadbent and coworkers[50-55] studied the catalytic activity of rhenium catalysts in the liquid-phase hydrogenation of over 100 organic compounds. The following rhenium compounds were used as catalysts: (A) rhenium black, prepared by reduction of Re_2O_7 *ex situ*; (B) rhenium black, prepared by reduction of Re_2O_7 *in situ*[50]; (C) Re_2O_3, reduced by sodium borohydride[51]; (D) the tetrahydropyran complex of Re_2O_7[52]; (E) $ReO_2 . 2.5H_2O$[53]; (F) ReO_3[54]; (G) $ReO.2H_2O$.[55] Optimum reduction conditions were identified (temperature, pressure, and time), and suitable solvents were chosen. The properties of these catalysts are compared in Table 1, which lists only cases in which the yield was practically quantitative.

It is evident from Table 1 that many of the rhenium catalysts have considerable activity. By choosing comparable hydrogenation conditions (temperature, reaction time, and pressure), the best catalysts can be identified. For example, the best catalyst for the reduction of hex-1-ene to hexane is *in situ* rhenium black (B); for the reduction of 2,4,4-trimethylpent-1-ene to 2,4,4-trimethylpentane, the tetrahydropyran complex of Re_2O_7 (D) and $ReO.2H_2O$ (G); for the reduction of maleic to succinic acid, *ex situ* rhenium black (A) and Re_2O_3 (C); for the reduction of the C=C double bond in the side chain of styrene to ethylbenzene, Re_2O_3 (C); for the reduction of cyclohexanone to cyclohexanol, $ReO.2H_2O$ (G); for the reduction of the N=N double bond in azobenzene to aniline, ReO_3 (F); for the reduction of the C=C double bond in cyclohexene to benzene and cyclohexane, ReO_3 (F); for the reduction of the C=C bond in the carbonyl group of crotonaldehyde to n-butanol, $ReO_2 . 2.5H_2O$ (E); for the reduction of butan-2-one to n-butanol, $ReO.2H_2O$ (G); for the reduction of ethyl benzoate to benzyl alcohol, *in situ* rhenium black (B); for the reduction of acetophenone to 1-phenylethanol, Re_2O_3 (C); for the reduction of ethyl acetate to ethanol, *in situ* rhenium black (B). The best catalyst for the reduction of the carbonyl group in acetic, octanoic, and dodecanoic acid to the corresponding alcohol is $ReO.2H_2O$ (G); for the reduction of hexanoic acid to n-decanol, *in situ* rhenium black (B); for the reduction of benzoic acid to toluene, $ReO.2H_2O$ (G); for the reduction of amino and nitro groups, and also hydrazobenzene to aniline, *ex situ* rhenium black (A). Conditions leading to the synthesis of various important alcohols from their corresponding acids have also been discovered[50] (see Table 1, No. 22-28).

From a comparison of the activity of rhenium catalysts with that of the conventional hydrogenation catalysts (Raney-Ni, PtO_2, and $CuCr_2O_4$), Broadbent concludes[50] that the rhenium catalysts are inferior to PtO_2 and Raney-Ni for the reduction of nitrobenzene to aniline, of styrene to ethylbenzene, and of cyclohexanone to cyclohexanol. However, the rhenium catalysts are unique in their ability to reduce acids to alcohols.

By using different catalysts based on rhenium oxide, other valuable products can be obtained. As Table 2 shows, Re_2O_3 reduced by sodium borohydride (C) can be used to reduce the C=C bond and the NO_2 group when chlorine or bromine atoms are present in the molecule (for example, *p*-chlorostyrene to *p*-chloroethylbenzene and *p*-bromonitrobenzene to *p*-bromoaniline); the tetrahydropyran complex of Re_2O_7, unlike other rhenium catalysts, allows the hydrogenation of the aromatic ring (see Table 2, compounds 6, 7, 9, 10). In the presence of $ReO_2 . 2.5H_2O$ (E) the olefin bond is reduced more rapidly than the carbonyl (14, 15) and the carboxyl group (16-18); ReO_3 (F) is an active catalyst for the reduction of various carboxylic acids (19-22) to the corresponding alcohols, and also of amides (28-30) to alkylamines. The ability of this catalyst selectively to reduce carboxyl groups without affecting the aromatic ring is also remarkable (26, 29, 30). It is evident from the examples given in Table 2 that the $ReO.2H_2O$ catalyst, prepared by reduction with alkali metals in ethylamine, is the most effective of the rhenium catalysts for the hydrogenation of carboxylic acids to alcohols (32-34), and for the reduction of nitro compounds to amines (39-42) and of ketones to alcohols (44-56).

Balandin and coworkers[56] obtained 100% yield in the hydrogenation of cyclohexene, octene, benzene, and acetone on a skeletal rhenium catalyst under a hydrogen

Table 1. Activity of rhenium catalysts towards the reduction of various organic compounds.

No.	Initial compound	Catalyst	Reaction conditions: solvent	t, °C	hydrogen pressure atm	time, h	Yield wt.%	Product
1	2	3	4	5	6	7	8	9
1	Hex-1-ene	B	none	100	156	2.5	100	n-Hexane
		C	none	68	220	7.0	100	
		B	none	154	200	2.0	100	
		F	none	95	205	15.0	100	
		G	none	119	200	2.5	100	
2	Hex-2-ene	C	none	110	239	4.0	100	n-Hexane
		D	none	122	245	3.0	100	
		G	none	151	200	3.0	100	
3	2,4,4-Trimethyl-pent-1-ene	C	none	140	252	2.5	100	2,4,4-Trimethylpentane
		D	none	91	218	3.0	100	
		G	none	200	200	0.5	100	
4	Maleic acid	A	Dioxan	148	177	2.5	100	Succinic acid
		B	none	196	286	12.0	91	
		C	Water	130	258	1.0	100	
		E	Petroleum ether	105	200	8.0	100	
5	Styrene	A	C_2H_5OH	108	156	3.5	100	Ethylbenzene
		B	C_2H_5OH	109	165	4.0	86	
		C	C_2H_5OH	25	194	6.0	100	
		C	C_2H_5OH	66	214	1.5	100	
		D	C_2H_5OH	107	255	2.0	100	
		E	C_2H_5OH	94	200	5.0	100	
		F	Cyclohexane	135	205	40.0	100	
6	Cyclohexanone	B	none	154	270	3.0	100	Cyclohexanol
		D	C_2H_5OH	113	248	5.0	100	
		E	none	115	200	12.0	100	
		G	none	119	200	2.5	100	
7	Azobenzene	B	none	125	249	24.0	92	Aniline
		F	none	195	205	15.0	96	
8	Cyclohexene	D	C_2H_5OH	151	264	13.0	100	Cyclohexane
		E	none	132	200	6.0	100	
		F	none	131	205	4.0	100	
		G	none	105	200	16.0	100	
9	Benzene	D	none	160	242	10.0	100	Cyclohexane
		E	none	177	200	14.0	100	
		F	none	240	205	4.0	100	
10	Crotonaldehyde	E	C_2H_5OH	148	200	8.0	100	n-Butanol
		F	Cyclohexane	147	205	16.0	100	
		G	C_2H_5OH	140	200	20.0	100	
11	Butan-2-one	E	none	100	200	4.0	100	Butan-2-ol
		C	none	72	217	3.0	100	
		G	none	100	200	2.5	100	
12	Ethyl benzoate	B	Cyclohexane	250	290	48.0	89	Benzyl alcohol
		F	ditto	237	205	80.0	93	
13	Acetophenone	A	C_2H_5OH	60	143	18.0	78	Methyl phenyl carbinol
		C	C_2H_5OH	150	255	1.0	100	
14	Ethyl acetate	B	none	148	191	11.0	100	Ethanol
		F	none	175	205	50.0	84	
15	Acetic acid	B	H_2O	150	168	10.0	100	Ethanol
		G	H_2O	145	200	4.5	100	
16	Octanoic acid	B	H_2O/dioxan	163	193	14.0	100	n-Octanol
		F	Cyclohexane	144	205	7.0	100	
		G	H_2O	173	200	5.0	100	
17	n-Decanoic acid	B	H_2O/dioxan	137	173	3.5	100	n-Decanol
		G	H_2O	173	200	6.0	100	
18	n-Dodecanoic acid	B	H_2O/dioxan	160	186	10	100	n-Dodecanol
		G	H_2O	177	200	7	100	
19	Benzoic acid	B	Benzene	254	190	15	91	Toluene
		G	H_2O	198	200	10	100	
20	Hydrazobenzene	B	Cyclohexane	185	280	42	97	Aniline
		F	ditto	185	205	33	100	
21	Nitrobenzene	A	C_2H_5OH	100	143	3	100	Aniline
		B	none	165	143	3	100	
		C	C_2H_5OH	75	195	4	100	
		F	none	226	205	25	100	
		G	none	106	200	7	100	
22	Trifluoroacetic acid	B	H_2O	207	300	18.5	100	Trifluoroethanol
23	Heptafluorooleic acid	B	H_2O	190	302	17	70	Heptafluorobutanol
24	Phenylacetic acid	B	none	149	160	14	78	2-Phenylethanol

Table 1 (contd.)

No.	Initial compound	Catalyst	Reaction conditions: solvent	t, °C	hydrogen pressure atm	time, h	Yield wt.%	Product
1	2	3	4	5	6	7	8	9
25	Lactic acid	B	none	150	258	8	84	Propylene glycol
26	Levulinic acid	B	none	106	150	18	71	β-Valeroacetone
27	β-Alanine	B	H_2O	250	210	32	92	Propanol
28	Glutaric acid	B	Dioxan	210	184	5	82	Pentane-1,5-diol
		B	H_2O	250	179	50	100	
29	*N*-Ethylacetamide	B	C_2H_5OH	245	352	22	96	*N,N*-Diethylaniline

pressure of 100–130 atm and temperature in the range 160–180°C. With this catalyst, the reduction of dimethyl maleate goes to completion even at room temperature and atmospheric pressure.

Platonov[46] was the first to note the interesting fact that rhenium catalysts can be activated by controlled amounts of typical catalyst poisons such as H_2S and As_2O_3. This effect was investigated in the particular case of ethanol dehydrogenation. At 500°, 30.7% of acetaldehyde and 0.9% of ethylene are formed from ethanol in the presence of a rhenium catalyst. On adding H_2S or As_2O_3 at a concentration of 0.004 mole per mole of ethanol the yields became (under otherwise identical conditions) 47.8 and 6.1% (with H_2S) and 43 and 3.8% (with As_2O_3) of aldehyde and ethylene respectively. With a further increase in the concentration of the poison to 0.008 mole per mole of alcohol, the yield of aldehyde falls off. Whereas formaldehyde is fully decomposed on a rhenium catalyst, the decomposition is suppressed[57] in the presence of H_2S or As_2O_3 (41.7 and 30.2% respectively of CH_2O are detected at 400°). The catalytic conversion of cyclohexanol yields mainly phenol[47], whereas in the presence of finely divided rhenium the main product is cyclohexanone. These observations led to an intensive study of the catalytic properties of rhenium sulphide.

The dehydrogenation of alcohols to aldehydes and ketones in the presence of rhenium sulphide was investigated by Platonov[58]. The products obtained from methanol, ethanol, and isopropanol (at 400, 550, and 500° respectively) contained 53.2, 53.5, and 91.4% of the appropriate aldehyde or ketone; cyclohexanol at 500° gave 78.8% of phenol and 6.7% of cyclohexanone. The interesting catalytic properties of rhenium sulphide are ascribed[58] to the similarity of its crystal lattice to that of MoS_2, which is extensively used as a catalyst for various reactions. Thus, formaldehyde, acetaldehyde, and acetone can be obtained in high yields from the corresponding alcohols by using ReS_2 as a catalyst.

The rhenium sulphides (ReS_2 and Re_2S_7) have been investigated by Broadbent and coworkers[59] as liquid-phase hydrogenation catalysts. The hydrogenations were carried out in a bomb containing 0.5 mole of the compound, a solvent, and 2.5 g of the catalyst per mole of the compound to be hydrogenated, under a pressure of hydrogen between 56 and 300 atm. The reaction conditions and the results obtained in the presence of rhenium heptasulphide and disulphide are listed in Table 3. The reductions obtained on Re_2S_7 include styrene to ethylbenzene, 1,1-methylphenylethanol (2-phenylpropan-2-ol) to cumene, maleic to

Table 2. Reduction of organic compounds in the presence of various rhenium catalysts with over 60% yield.

No.	Initial compound	Solvent	Temp., °C	Pressure atm	Reaction time, h	Yield, wt.%	Reaction product	Catalyst
1	*p*-Chlorostyrene	C_2H_5OH	34	197	11.0	100	*p*-Chloroethylbenzene	Re_2O_3 (C)
2	Pentan-3-one	C_2H_5OH	90	220	4.0	89	Pentan-3-ol	Re_2O_3 (C)
3	*p*-Bromonitrobenzene	C_2H_5OH	124	222	5.5	100	*p*-Bromoaniline	Re_2O_3 (C)
4	Capronitrile	none	240	306	7.0	69	Trihexylamine	Re_2O_7 (D)
5	Isobutyric acid	none	255	311	3.0	70	Isobutanol	Re_2O_7 (D)
6	Toluene	none	174	242	15.0	100	Methylcyclohexane	Re_2O_7 (D)
7	Cumene	none	148	255	11.0	71	Isopropylcyclohexane	Re_2O_7 (D)
8	t-Butylbenzene	none	195	272	9.0	100	t-Butylcyclohexane	Re_2O_7 (D)
9	*p*-Xylene	none	162	240	3.0	89	1,4-Dimethylcyclohexane	Re_2O_7 (D)
10	Phenol	Cyclohexane	170	260	15.0	92	Cyclohexanol	Re_2O_7 (D)
11	4-Nitrophenyl ether	none	160	240	3.0	100	4-Aminodiphenyl ether	Re_2O_7 (D)
12	Diphenylmethane	none	208	274	9.0	70	Cyclohexylphenylmethane	Re_2O_7 (D)
13	Acetophenone	none	143	200	8.0	64	1-Phenylethanol	$ReO_2 \cdot 2.5H_2O$ (E)
14	Hex-5-en-2-one	none	166	200	6.0	100	Hexan-2-ol	$ReO_2 \cdot 2.5H_2O$ (E)
15	2-Allylcyclohexanone	none	168	200	10.0	72	2-Propylcyclohexanone	$ReO_2 \cdot 2H_2O$ (E)
16	Crotonic acid	Petroleum ether	188	200	7.0	68	Butyl butyrate	$ReO_2 \cdot 2H_2O$ (E)
17	Vinylacetic acid	ditto	161	200	12.0	100	Butyric acid	$ReO_2 \cdot 2H_2O$ (E)
18	Levulinic acid	none	152	200	12.0	100	γ-Valerolactone	$ReO_2 \cdot 2H_2O$ (E)
19	Butyric acid	Cyclohexane	144	205	10.0	100	n-Butanol	ReO_3 (F)
20	Crotonic acid	H_2O	146	205	10.0	80	n-Butanol	ReO_3 (F)
21	Valeric acid	none	145	205	11.0	75	n-Pentanol	ReO_3 (F)
22	Undecylenic acid	H_2O	156	205	12.0	100	n-Undecanol	ReO_3 (F)
23	n-Butyl butyrate	none	218	205	28.0	100	n-Butanol	ReO_3 (F)
24	Pentan-3-one	none	161	205	1.0	100	Pentan-3-ol	ReO_3 (F)
25	Butan-2,3-diol	C_2H_5OH	204	205	10.0	73	Butan-2,3-diol	ReO_3 (F)
26	Benzaldehyde	Cyclohexane	124	205	20.0	88	Benzyl alcohol	ReO_3 (F)
27	Nitrocyclohexane	none	234	205	36.0	68	Cyclohexylamine	ReO_3 (F)
28	Acetamide	Cyclohexane	200	205	18.0	88	Ethylamine	ReO_3 (F)
29	Benzamide	C_2H_5OH	220	205	49.0	69	Benzylamine	ReO_3 (F)
30	Acetanilide	Cyclohexane	185	205	31.0	71	*N*-ethylaniline	ReO_3 (F)
31	Hex-5-en-2-one	C_2H_5OH	81	200	6.0	72	Hexan-2-one	$ReO \cdot 2H_2O$ * (G)
32	Propionic acid	H_2O	162	200	6.0	100	n-Propanol	ReO_3 (F)
33	Isobutyric acid	H_2O	172	200	5.0	95	Isobutanol	ReO_3 (F)
34	Valeric acid	H_2O	168	200		87	Pentanol	ReO_3 (F)
35	1-Phenylbut-2-ene	none	171	200	2.5	100	Butylbenzene	ReO_3 (F)
36	Pyridine	C_2H_5OH	205	200	7.0	100	Piperidine	ReO_3 (F)
37	Hex-5-en-2-one	C_2H_5OH	68	200	10.0	91	Hexan-2-one	$ReO \cdot 2H_2O$** (G)
38	2-Allylcyclohexanone	C_2H_5OH	125	200	6.0	73	2-Propylcyclohexanone	$ReO \cdot 2H_2O$* (G)
39	Nitrocyclohexane	C_2H_5OH	120	200	7.0	100	Cyclohexylamine	$ReO \cdot 2H_2O$ (G)
40	*m*-Nitroacetophenone	C_2H_5OH	110	200	24.0	100	*m*-Aminoacetophenone	$ReO \cdot 2H_2O$ (G)
41	*m*-Nitrostyrene	C_2H_5OH	118	200	1.0	100	*m*-Aminostyrene	$ReO \cdot 2H_2O$ (G)
42	*m*-Nitrobenzaldehyde	C_2H_5OH	124	200	10.0	100	*m*-Aminobenzaldehyde	$ReO \cdot 2H_2O$
43	Propynol	C_2H_5OH	142	200	2.5	77	n-Propanol	$ReO \cdot 2H_2O$
44	Acetone	—	78	200	10.0	100	Propan-2-ol	$ReO \cdot 2H_2O$ (G) ***
45	3-Methylbutan-2-one	—	198	200	7.0	100	3-Methylbutan-2-ol	$ReO \cdot 2H_2O$ (G)
46	Pentan-2-one	—	136	200	11.0	100	Pentan-2-ol	$ReO \cdot 2H_2O$ (G)
47	Pentan-3-one	—	160	200	6.0	100	Pentan-3-ol	$ReO \cdot 2H_2O$ (G)
48	4-Methylpentan-2-one	—	180	200	5.0	100	4-Methylpentan-2-ol	$ReO \cdot 2H_2O$ (G)
49	Hexan-2-one	—	135	200	11.5	100	Hexan-2-ol	$ReO \cdot 2H_2O$ (G)
50	Hexan-2,5-dione	—	121	200	10.5	95	Hexan-2,5-diol	$ReO \cdot 2H_2O$ (G)
51	Heptan-2-one	—	172	200	3.5	96	Heptan-2-ol	$ReO \cdot 2H_2O$ (G)
52	Heptan-3-one	—	152	200	5.0	100	Heptan-3-ol	$ReO \cdot 2H_2O$ (G)
53	Heptan-4-one	—	186	200	2.0	98	Heptan-4-ol	$ReO \cdot 2H_2O$ (G)
54	Cycloheptanone	—	175	200	8.5	100	Cycloheptanol	$ReO \cdot 2H_2O$ (G)
55	Octan-2-one	—	130	200	6.0	86	Octan-2-ol	$ReO \cdot 2H_2O$ (G)
56	Nonan-2-one	—	178	200	6.0	100	Nonan-2-ol	$ReO \cdot 2H_2O$ (G)

* Reduced by lithium ethylamide
** Reduced by lithium in liquid ammonia
*** Reduced by sodium in liquid ammonia

succinic acid, nitrobenzene to aniline, *p*-bromonitrobenzene to *p*-bromoaniline, allyl phenyl sulphide to propyl phenyl sulphide, diphenyl disulphide to thiophenol. The carbonyl double bond (acetophenone) is reduced less readily than the carbon–carbon double bond (styrene). The C–S bond is not broken during the hydrogenation of organosulphur compounds. Thus, allyl phenyl sulphide gives only propyl phenyl sulphide, diphenyl disulphide gives only thiophenol, thiophen gives only thiophane. If the reaction is carried out under more drastic conditions, for example at 300°, cyclohexane and benzene are formed from the thiophenol, and benzene is formed from the diphenyl disulphide. The nitro group is readily reduced at or just above room temperature. Rhenium disulphide is less active than the heptasulphide. The activity of rhenium sulphide catalysts towards a number of reactions was compared with the activity of the existing catalysts molybdenum sulphide and cobalt sulphide[59]. The most active hydrogenation catalyst was found to be Re_2S_7, followed by ReS_2, MoS_2, and CoS_x (in that order). Cobalt polysulphide has a high activity (comparable to that of Re_2S_7) only in the reduction of nitrobenzene to aniline.

Thus, Re_2S_7 has been shown to be an active liquid-phase hydrogenation catalyst. It induces quantitative reduction of styrene, cyclohexene, maleic acid, nitrobenzene, *p*-bromonitrobenzene, and diphenyl sulphide.

Balandin and coworkers[60] studied the catalytic reduction of chloronitrobenzenes in the presence of Re_2S_7 (in amounts between 2 and 10% of the weight of chloronitrobenzene) at 100–123° and for reaction times of 40–60 h. *p*-Chloronitrobenzene, 3,4-dichloronitrobenzene, and 2,4,5-trichloronitrobenzene gave the corresponding chloroanilines in 100% yield (measured chromatographically).

The catalytic reduction of functional groups in sulphur compounds is difficult to realise, because all known catalysts are susceptible to catalytic poisoning (to a greater

or lesser extent) by sulphur in the bivalent state. However, Re_2S_7 proved to be very active even under these conditions[61].

Aretos and Viall[62] reduced 2-nitrothiophen to 2-acetylaminothiophen at 100° in the presence of acetic anhydride:

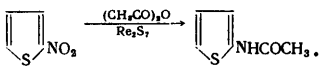


Table 3. Hydrogenation in the presence of sulphide catalysts.

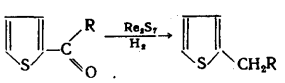
Initial compound	Amount of catalyst, g/mole of initial cpd.	Solvent	Pressure, atm	Temperature, °C	Time, h	Reduction product	Yield, %
			Re_2S_7 catalyst				
Styrene	2.5	C_2H_5OH	120	100-135	1	Ethylbenzene	100
Phenylacetylene	2.5	C_2H_5OH	133	106-135	1.75	Ethylbenzene	70
2-Phenylpropan-2-ol	2.5	C_2H_5OH	140	130	0.33	Cumene	100
Cyclohexene	0.5	C_2H_5OH	140	240	3	Cyclohexane	92
Maleic acid	1.0	H_2O	91	150	5	Succinic acid	100
Acetophenone	2.5	C_2H_5OH	160	216-230	0.17	Ethylbenzene	85
Nitrobenzene	2.5	C_2H_5OH	133	25	6	Aniline	100
Nitrobenzene	2.5	C_2H_5OH	133	60-100	0.5	Aniline	100
p-Bromonitrobenzene	2.5	Methyl cellosolve	133	60	0.5	*p*-Bromoaniline	100
Bromobenzene	2.5	ditto	190	225-250	3	Bromobenzene	89
						Benzene	11
Pentyl phenyl sulphide	2.5	C_2H_5OH	133	150-160	0.5	Propyl phenyl sulphide	100
Diphenyl sulphide	2.5	none	160	280-300	2	Benzene	94
Diphenyl disulphide	2.5	Methyl cellosolve	154	165-195	1	Thiophenol	100
Thiophen	2.5	none	140	230-260	3.75	Thiophane	70
						Butanthiol	0
			ReS_2 catalyst				
Styrene	1.0	C_2H_5OH	140	150-180	1	Ethylbenzene	63
Nitrobenzene	0.5	C_2H_5OH	125	110-200	2	Aniline	94
Allyl phenyl sulphide	2.5	C_2H_5OH	160	240-245	1	*p*-Propyl phenyl sulphide	91

The thiophen ring was hydrogenated at 200°, giving thiophane and 2-methylthiophane. Various 1,2-dithiol-3-thionones have also been hydrogenated at 180-200°:



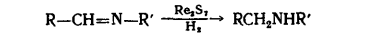
where R = 4-C_6H_5, 5-C_6H_5, and 5-*p*-$CH_3OC_6H_4$. In every case, ring opening was observed, with formation of benzene and a thiol.

Ryashentseva and coworkers[63,64] achieved selective reduction of the carbonyl group in a series of thiophen compounds. In the presence of rhenium heptasulphide, they obtained 2-methylthiophen and 2-ethylthiophen (in 50 and 80% yield respectively) from 2-thiophenal and 2-acetothienone in dioxan under autoclave conditions (170-190°, 100-130 atm hydrogen pressure):

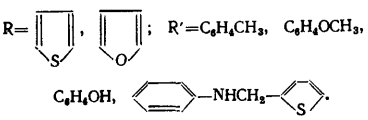


where R = H, CH_3.

The same workers[65,66] also found conditions leading to the selective hydrogenation of the azomethine group (-C=N-) without attacking the thiophen or aromatic ring. Thus, they prepared the appropriate secondary amines from *N*-thienylidene-*p*-toluidine, *N*-thienylidene-*p*-anisidine, *N*-thienylidene-*p*-aminophenol, *N*-furfurylidene-*p*-toluidine, and *N,N'*-dithienylidene-*p*-phenylenediamine:

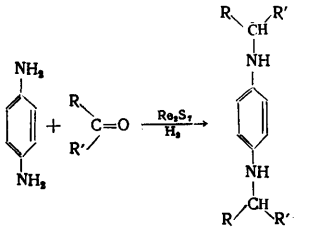


where

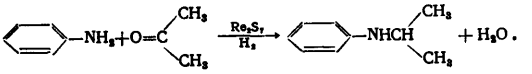


Conditions for the reduction of azomethines to secondary amines in the presence of 100 mg Re_2S_7 in dioxan, and under a hydrogen pressure of 130 atm, are summarised in Table 4. It is evident that the presence of *p*-toluidine, *p*-anisidine, or *p*-aminophenol groups has practically no effect on the selectivity of the hydrogenation of the azomethine group: reduction takes place at 150-170° in 3 h in the presence of 1.5-2 g Re_2S_7 per mole of the azomethine. If the thiophen residue is replaced by furan in the original azomethine, the hydrogenation (under otherwise comparable conditions) is hindered, and the yield of secondary amines drops to ~40%. It has been shown that the catalyst can be re-used a number of times.

Ryashentseva and coworkers[67,68] studied the alkylation of *p*-phenylenediamine and its hydroquinone complex by ketones (acetone, ethyl methyl ketone, and cyclohexanone) in the presence of Re_2S_7. Reaction took place, in a rotating autoclave, at 150-200° and under 100-130 atm hydrogen pressure, in 2.5-3 h. *N,N'*-di-isopropyl-, *N,N'*-di-isobutyl-, and *N,N'*-dicyclohexyl-*p*-phenylenediamine were obtained in 60-94% yield, as well as their hydroquinone complexes. The best results were obtained by using a three-fold excess of the ketone. Alkylation takes place by the scheme



Dovell and Greenfield[69] used rhenium heptasulphide for the reductive alkylation of aniline by acetone to give *N*-isopropylaniline:



The alkylation took place in an autoclave at 140° and 80-100 atm hydrogen pressure. After 4.4 h, *N*-isopropylaniline was obtained in 90% yield (measured by gas-liquid chromatography).

These results show that the reductive alkylation of aromatic amines in the presence of rhenium heptasulphide is not accompanied by hydrogenation of the benzene ring, cleavage of the C=N bond, or reduction of the ketone. Rhenium heptasulphide was the most active of all the sulphide catalysts examined[68,69] in this particular reaction.

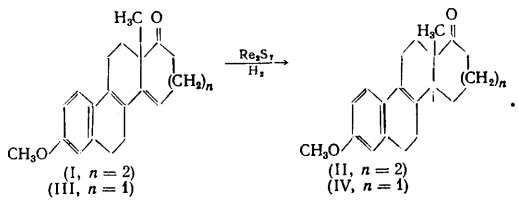
Platonova and coworkers[70] were able to reduce the double bond in a series of steroid compounds in the presence of Re_2S_7. Thus, they isolated in ~15% yield the methyl ether of *d,l-D*-homo-$\Delta^{1,3,5,8(8)}$-oestrapentaene-one-17a (II), with a *cis* configuration of the *C* and *D* rings, from the methyl ether of *d,l-D*-homo-$\Delta^{1,3,5(10),8,14}$-oestrapentaenone-17a (I) in benzene and under hydrogen pressure.

Table 4.

Initial compound, g	Reaction temp., °C	Yield of products, %	
		secondary amine	primary amine
N-thienylidene-*p*-toluidine (Ref.10)	170[a]	55	10
	170[b]	60	10
N-thienylidene-*p*-anisidine (Ref.10)	150	55	10
	200	20	60
N-thienylidene-*p*-aminophenol (Ref.5)	150	60	
N-furfurylidene-*p*-toluidine (Ref.10)	150	39	10
	150[c]	40	12
	150[d]	40	13
	150[e]	25	14
	150[f]	29	14
N,N'-dithienylidene-*p*-phenylene-diamine (Ref.5)	170	22	

[a] Pressure 125 atm; [b] Pressure 170 atm; [c] Re_2S_7 150 mg; [d] Re_2S_7 200 mg; [e] in benzene; [f] in n-hexane.

In a similar way, the methyl ether of $\Delta^{1,3,5(10),8}$-oestratetraenone-17 (IV) was obtained in 40% yield from the methyl ether of $\Delta^{1,3,5(10),8,14}$-oestrapentaenone-17 (III). Products of the partial and the complete reduction of the keto group in position 17 were isolated and identified among the side-products:



(I, $n = 2$) (III, $n = 1$) (II, $n = 2$) (IV, $n = 1$)

Broadbent and Whittle[71] showed that Re_2Se_7 can also be a good hydrogenation catalyst at 100–240° and 200–300 atm pressure, with or without a solvent. Hydrogenation conditions and yields (which sometimes exceed 70%) are listed in Table 5.

It is evident from Table 5 that the C=O bond is saturated more readily than the C=C bond in the presence of Re_2Se_7, unless the latter is associated with other double bonds. Hydrogenation of the C=C bond in thiophen and in allyl phenyl sulphide proceeds without rupture of the C–S bond. By studying the reduction of *p*-bromonitrobenzene it was shown that the carbon–halogen bond is also unattacked whilst the nitro group is easily reduced. The benzene ring is fairly resistant to hydrogenation: only 4.5% of cyclohexane is formed from benzene.

Table 5. Hydrogenation in the presence of Re_2Se_7.

Initial compound	Solvent	Pressure atm	Temp., °C	time, h	Hydrogenation product	Yield, %
Nitrobenzene	C_2H_5OH	240	155	1.25	Aniline	100
Nitrobenzene	none	240	150	4.0	Aniline	100
Sodium *p*-nitrophenate	H_2O	226	130	1.0	*p*-Aminophenol	100
Nitropropane	C_2H_5OH	242	115	3.0	Propylamine	100
2,4,4-Trimethylpent-1-ene	none	287	200	5.0	Iso-octane	93.5
Cyclohexene	C_2H_5OH	306	200	3.0	Cyclohexane	40.0
Styrene	C_2H_5OH	246	135	2.0	Ethylbenzene	94.0
Crotonic acid	none	262	150	8.0	Butyric acid	100.0
Maleic acid	H_2O	207	60	7.0	Succinic acid	100.0
Maleic acid	Dioxan	265	150	0.75	Succinic acid	100.0
Cinnamic acid	Dioxan	260	145	2.5	Hydrocinnamic acid	100.0
Pentyl phenyl sulphide	C_2H_5OH	292	195	2.0	*p*-Propyl phenyl sulphide	100.0
Phenylacetylene	C_2H_5OH	268	100	1.0	Ethylbenzene	73.6
					Polymer	26.4
Thiophen	none	322	250	13.0	Thiophane	100.0
Butanone	none	238	105	5.0	Butan-2-ol	100
Cyclohexanone	C_2H_5OH	266	155	9.0	Cyclohexanol	100
Acetophenone	C_2H_5OH	248	150	2.25	Ethylbenzene	88
					1-Phenylethanol	10
p-Nitrobromobenzene	C_2H_5OH	235	100	3.0	*p*-Bromoaniline	100
2-Phenylpropan-2-ol	C_2H_5OH	264	160	1.1	Cumene	100
Benzyl phenyl sulphide	C_2H_5OH	326	190	7.0	Benzene	100
					Toluenethiol	100

Comparing the activity of Re_2Se_7 towards hydrogenation reactions with the activity of rhenium, molybdenum, and cobalt sulphides we find[59] that Re_2Se_7 is second only to Re_2S_7, but is much more active than molybdenum and cobalt sulphides. In the reduction of nitrobenzene it was shown that the Re_2Se_7 catalyst is unaffected by nitrogen, phosphorus, sulphur, selenium, and tellurium compounds, but is sensitive to arsenic compounds.

III. SUPPORTED RHENIUM CATALYSTS (dehydrogenation of alcohols, rearrangement of hydrocarbons, and treatment of petroleum fractions)

Platonov and coworkers[41,48] prepared a rhenium catalyst on a ceramic carrier containing a large proportion of alumina by a modified "nitric acid" method. The catalyst was shown to have a high selectivity towards the dehydrogenation of ethanol to acetaldehyde. However, the yield of acetaldehyde was only 14% at 600°.

In Balandin's laboratory, rhenium catalysts were prepared[72] by impregnating the carrier (active carbon, alumina, asbestos, or quartz) with solutions of ammonium perrhenate or of the rhenium–dioxan complex ($Re_2O_7.C_4H_8O_2$).[73] The highest activity was found in the rhenium catalysts supported on carbon, prepared by the dioxan method[72,74]. Transformations of primary and secondary alcohols (ethanol, n-propanol, isopropanol, and s-butanol) were investigated. Isopropanol at 150–200° gave acetone with a yield approaching the maximum thermodynamically possible value. The dehydrogenation of primary alcohols is complicated by the formation of esters and by decarbonylation of the resulting aldehyde. The intermediate product in the formation of γ-butyrolactone from 1,4-butandiol is γ-hydroxyoleic aldehyde.

Balandin, on the basis of the structural correspondence principle of the multiplet theory of catalysis, was the first to suggest the possibility of dehydrogenation of six-membered rings by a sextet mechanism on rhenium, since the latter has hexagonal symmetry.

Balandin and coworkers[75] studied the dehydrogenation kinetics of cyclohexane, methylcyclohexane, and ethylcyclohexane on rhenium catalysts supported on carbon. The rate of dehydrogenation decreases with increase of molecular weight of the hydrocarbon. The same workers[75] investigated the dependence of catalyst activity and activation energy for the dehydrogenation of cyclohexane upon the rhenium content of the catalyst. An activation energy of 12.8 kcal mole^{-1} was found to correspond to a rhenium content of 30 wt.% in the catalyst. It was also shown that the relative benzene adsorption coefficient is independent of the reaction temperature. The dehydrogenation of cyclohexane on rhenium is a zero-order reaction. The carbon-supported rhenium catalyst develops its highest activity during the first few minutes of the reaction[76]. Thus, the yield of benzene from cyclohexane at 360–380° is 90–95% after the first 5–7 min. Subsequently, the activity falls to a constant value at some intermediate level. The catalyst is regenerated by hydrogen treatment at 500° for 1–1.5 h. The authors[76,77] offer an explanation of the effect of the carrier on the activity of the catalyst in this reaction. They suggest that rhenium on carbon is similar to platinum on carbon, and should be an active dehydrogenation catalyst for cyclohexane under conditions of energy correspondence: this prediction is confirmed by experiment. However, their explanation of the results obtained with rhenium–alumina catalysts is less convincing, and is inconsistent with other experimental results[78–81]. Thus, according to Balandin, the ratio of M–M to O–O interatomic distance is: for Pt, 2.77/2.64 = 1.05; for Re, 2.736/2.64 = 1.035; for Ni, 2.48/2.64 = 0.94. The corresponding deviations from the integral value of 1 are: +5% for Pt, +3.5% for Re, and –6.4% for Ni. They conclude that negative deviations are favourable, and therefore that Ni on Al_2O_3 should be the most active catalyst. With rhenium the correspondence between interatomic distances is fairly good, but the deviation (though small) is positive, and therefore the rhenium lattice is under compression and the catalytic activity is low (the yield of benzene from cyclohexane is 5–7% with a Re/Al_2O_3 catalyst). But according to this argument the activity of the platinum–alumina catalyst (the industrial platinum forming catalyst) should be negligible. The authors ascribe the activity of this catalyst to the state of the platinum. They postulate relatively large Pt crystals, insensitive to the influence of the carrier, even though platinum forming catalysts are known to contain only 0.3–0.5% of platinum on alumina.

Balandin and coworkers[76] also studied the dehydrocyclisation of n-heptane on a rhenium–carbon catalyst. At 468°, and with a flow of n-heptane of 0.173 ml min^{-1}, the product contains 14.0% of aromatic hydrocarbons and 9.4% of unsaturated compounds. Later they examined the properties of a rhenium–carbon catalyst made by the dioxan method[56] and containing 30% of rhenium. On this catalyst, complete reduction of cyclohexene to cyclohexane and of acetone to isopropanol was obtained in 1–2 h at 160–180° and 70–110 atm hydrogen pressure; cinnamic aldehyde was quantitatively reduced to hydrocinnamic alcohol at 250° and 110–130 atm pressure.

It was also shown[82] that the rate of dehydrogenation of cyclohexane on a rhenium–carbon catalyst is higher than the rate of dehydrogenation of cyclohexene, and therefore that cyclohexene cannot be an intermediate in the transformation of cyclohexane to benzene.

Isagulyants and coworkers[83] studied the mechanism of conversion of cyclohexane and of cyclohexene at 270–400° at atmospheric pressure in the presence of the same catalyst. They showed that cyclohexene is not a precursor in the formation of benzene from cyclohexane: benzene is formed directly from cyclohexane. This conclusion is consistent with the earlier observations[82] from the same laboratory.

Ryashentseva and Minachev[84–88] studied the properties of rhenium catalysts with special reference to the reactions of C_5–C_7 hydrocarbons under reforming conditions.

Metals in the neighbouring groups of the Periodic Table (VI and VIII) have been studied intensively from this point of view, and some of them have found application in various industrial processes (in particular, petroleum refining).

The reactions of hydrocarbons have been used to study the properties of rhenium catalysts as a function of metal content, nature of the carrier, specific surface area, catalyst treatment, and reaction conditions. The experiments were made in a flow reactor under pressure of hydrogen. The products of catalysis were analysed by gas–liquid chromatography. Ryashentseva and Afanas'eva[84] developed a procedure for extracting the rhenium from rhenium–alumina and rhenium sulphide–alumina catalysts, using 5% HNO_3 and HNO_3–H_2O_2 mixtures respectively, followed by a photometric determination.

Catalysts containing 20% of rhenium were found to be the most active of the rhenium–alumina catalysts[79]. At 380°, 5 atm hydrogen pressure, and a feed rate of 1.0 h^{-1} [litre h^{-1}? (Ed. of Translation)] (5 : 1 ratio of hydrogen to hydrocarbon), up to 80% of benzene was obtained from cyclohexane during the first few hours' operation, but the activity of the catalyst decreased with time, and after 21 h the product contained only 5% of benzene. Methylcyclopentane and n-hexane under the same conditions undergo mainly hydrogen cracking. Convincing results were obtained with a catalyst containing 5% of rhenium on zeolite. In this system, high selectivity for the cyclohexane dehydrogenation reaction is observed.

Treatment of the rhenium–alumina catalysts with hydrogen sulphide[85] increases their activity. As in the case of the rhenium–alumina catalysts themselves, the activity increases with rhenium content. For example, for catalysts treated with hydrogen sulphide and containing 1, 5, 10, 15, and 20% of rhenium the yield of benzene from cyclohexane is 2.9, 20, 31, 34, and 76% respectively. The catalyst containing 20% of rhenium is the most active. At 500°, 5 atm hydrogen pressure, and 5 : 1 hydrogen to hydrocarbon ratio, this catalyst gives up to 80% of benzene from cyclohexane, and 53% of benzene from methylcyclopentane. Under the same conditions, n-hexane suffers appreciable cracking, but the product contains 10% of aromatic hydrocarbons, indicating some measure of dehydrocyclisation.

Prinzler and Klotzsche[89] studied the dehydrogenation of cyclohexane to benzene, the dehydrocyclisation of n-heptane to toluene, the isomerisation of n-pentane to isopentane, and the demethylation of toluene to benzene on $Re–Al_2O_3$ and $Re–Al_2O_3.SiO_2$ catalysts at atmospheric pressure and 480–490°. They showed that in these reactions the rhenium catalysts are much less active than the platinum–alumina catalysts. At feed rates of 0.5–5.0 changes per hour, 5% of benzene is formed from cyclohexane and only 1.7% of toluene from n-heptane. Addition of ZnO_2 to these catalysts does not raise their activity.

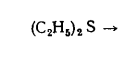
Müller and Wencke[90] studied the effect of different carriers on the catalytic properties of rhenium catalysts. They examined two modifications of alumina (α and γ) and beech charcoal. The chosen model reaction was the gas-phase dehydrogenation of cyclohexane between 250 and 420° at ~50% conversion. Rhenium on α-Al_2O_3 had the

highest catalytic activity. Rhenium deposited on γ-Al_2O_3 shows the same activity only at much higher concentrations of the metal. The authors conclude that α-Al_2O_3 is a better carrier than γ-Al_2O_3 at low concentrations of rhenium; beech charcoal occupies an intermediate position.

Müller and Wencke offer the following explanation of their findings. The pure carriers have different BET surfaces: 939, 143, and 8 $m^2 g^{-1}$ for beech charcoal, γ-Al_2O_3, and α-Al_2O_3 respectively. Since α-Al_2O_3 has the smallest surface, catalytically active groupings of atoms can form on it at quite low metal concentrations ($\sim$0.5%). γ-Al_2O_3 requires a higher metal concentration to achieve the same condition. Beech charcoal, which has the largest surface area, should become catalytically active at significantly higher concentrations of the metal than is found in practice. The discrepancy is ascribed to the possibility of epitaxial growth, on the assumption that surface formations on the charcoal can lead to dehydrogenation of cyclohexane as well as the octahedral surface of the rhenium lattice.

Blackham and coworkers[91] studied the properties of rhenium–alumina catalysts as a function of the method of preparation of the catalyst in the dehydrocyclisation of n-heptane at 550–600° under atmospheric pressure. Rhenium catalysts are inferior to platinum catalysts in this reaction. Thus, up to 80% of dehydrocyclisation products are obtained with a 1% Pt–Al_2O_3 catalyst under optimum conditions, as compared with $\sim$60% on a 5% Re–Al_2O_3 catalyst. Rhenium–alumina catalysts prepared by different methods had comparable activities.

Rhenium catalysts have been investigated[92] in the dehydrocyclisation of diethyl sulphide to sulphide to thiophen under 3 atm hydrogen pressure, apparent contact time 0.6 s, catalyst particle size 1–1.5 mm, and 15 wt.% concentration of the sulphide in helium:

$$(C_2H_5)_2S \rightarrow \text{} + 3H_2 .$$

The activity of rhenium catalysts in this reaction was found to be similar to that of other dehydrocyclisation catalysts, such as chromium and molybdenum. In the presence of rhenium, the dehydrocyclisation reaction is complicated by decomposition of the sulphide at the C–S bond, and the yield of thiophen is no more than 13% of the initial diethyl sulphide.

Sokolova and coworkers[60] obtained the appropriate chloroanilines in 100% yield from *p*-dichlorobenzene and trichlorobenzene in the presence of a 5% Re_2S_7–SiO_2 catalyst at 120–140° and 40–65 h reaction time.

The use of rhenium catalysts in the treatment of petroleum fractions at high temperatures in the presence of a pressure of hydrogen has been investigated[80,81,93].

A Patent by Hummel[80] discloses that the fraction boiling at 100–180°, containing 14% of aromatic hydrocarbons and having an octane number of 53, can be dehydrogenated at 475–500° under 50 atm pressure to give a 49% content of aromatics and an octane number of 71. The catalyst was prepared from a rhenium salt solution containing 3 g $litre^{-1}$ of rhenium, deposited on activated alumina to which 0.3% of fluoride and 0.1% of MgO had been added. Before the reaction, the catalyst was activated by hydrogen reduction at 475°. The preparative details of the catalyst are not disclosed in the Patent. It is shown[80] that the rhenium catalyst leads to isomerisation as well as to the formation of aromatic hydrocarbons from n-alkanes, and is more effective than platinum catalysts in this respect.

The same author[81] subsequently proposed the rhenium–alumina–silica catalyst for the production of liquid fuels from high-boiling hydrocarbon oils, jellies, and petroleum products under 100–700 atm pressure and at temperatures between 300 and 450°.

Lüder and Drescher[93] studied the application of rhenium catalysts in hydrogenation and reforming processes. The experiments were made with a fraction containing 13.6% of aromatic hydrocarbons, 43.5% of naphthenes, and 42.9% of alkanes. Rhenium catalysts on alumina were inferior to the industrial molybdenum and platinum catalysts, which gave 54% of aromatic hydrocarbons from the experimental fraction as compared with only 22% using the rhenium–alumina catalyst. Replacement of the NH_4ReO_4 by $KReO_4$ did not improve the aromatising properties of the catalyst. The authors succeeded in raising the content of aromatics to 32–36% and the octane number to 72–74 by using much higher proportions of rhenium in the catalyst and by including small amounts of MgO and fluorides.

Additions of iron had no effect, even in the presence of large amounts of rhenium. By varying the preparative conditions of the catalyst, up to 50% of aromatic hydrocarbons can be obtained in the reforming products, but the overall yield of liquid products is significantly decreased by the formation of gaseous hydrocarbons. However, a rhenium dehydrogenation catalyst for hydrocarbons boiling in the benzine range could not be prepared. Good results were obtained by treating a middle prehydrogenation oil with a rhenium catalyst supported on Fuller's earth. The rhenium content was 3 g $litre^{-1}$, corresponding to 0.4–0.5 wt.% (as compared with 5–10 wt.% in the hydrogenation media used in industrial catalysts). The rhenium was used as the metal or the sulphide. The authors[93] observed extensive fission of the oils: the yield of the fraction boiling up to 200° was 82%. Better results were obtained with a catalyst of composition 3 g $litre^{-1}$ supported on Fuller's earth treated with fluorides. The octane number of the reforming products obtained with an industrial catalyst was 60.1, whereas the rhenium catalyst gave a higher value (74.8). The catalyst was tested during 1150 h. A Diesel fraction gave a reforming product with cetane rating 45 and 47. However, the high initial activity of the rhenium catalysts falls off quite rapidly. If this shortcoming could be overcome, the rhenium catalyst would offer interesting possibilities for the treatment of middle oil fractions. The authors believe that rhenium catalysts will find industrial applications, but that more research is needed into their regeneration and into more general applications.

Minachevich and Ryashentseva[87] showed that between 32 and 47% of aromatic hydrocarbons can be obtained from the direct-distillation benzine fraction of b.p. 38.5–196°, containing 10% of aromatic hydrocarbons, by reforming with a 20% Re–Al_2O_3 catalyst (treated with hydrogen sulphide) at 480–490°, 5 atm pressure, flow rate 1.0 changes per hour, and 5 : 1 ratio of H_2 to hydrocarbons. The octane number (without tetraethyllead) increases from 47.8 to 71 and 87.2. Reforming of the benzine fraction (b.p. 89.5–126°) from the Volga–Urals region[87] increased the content of aromatics from 6 to 20–60%, and lowered the content of sulphur compounds from 0.017 to 0.002–0.007%. This catalyst was studied during 500 h, including 5 regenerations. Although the aromatising power of the catalyst was effectively restored after each regeneration, the stability gradually deteriorated. The yield of aromatic hydrocarbons during the first 30 h was 55–60%; subsequently the activity began to fall off, and after 60 h operation the content of aromatics was only $\sim$20%. This level

of activity was retained for approximately 100 h, but after this period the activity decreased and the content of aromatic hydrocarbons fell to 12%.

Hence, the rhenium catalysts cannot compete with the industrial platinum catalysts as regards stability. Furthermore, their rhenium content must be much higher than the platinum content of conventional platinum forming catalysts.

IV. MIXED RHENIUM CATALYSTS (liquid-phase hydrogenation, rearrangement of hydrocarbons, and reforming of light petroleum fractions)

Sokol'skii and coworkers[94-99] studied the effect of adding rhenium on the activity and selectivity of various nickel catalysts for liquid-phase hydrogenation.

They investigated the hydrogenation of unsaturated compounds containing ethylene, acetylene, and aldehyde bonds, on nickel–silica catalysts, and showed[94] that the rate of hydrogenation is increased by adding up to 5% of rhenium to the catalyst. Higher rhenium contents degrade the activity of the catalyst. Very small additions of rhenium (<0.5%) were also found to deactivate the catalyst. By adding an alcoholic solution of potassium perrhenate to a Raney nickel catalyst, they were able to hydrogenate tetramethylbutynediol, vinyl ether, cinnamaldehyde, and vinylethynyldimethyl carbinol (2-methylhex-3-yne-5-ene-2-ol) in the liquid phase and to demonstrate the promoting action of potassium perrhenate. Addition of rhenium to the catalyst not only increases the rate of hydrogenation of unsaturated compounds, but also extends the useful life of the catalyst. For example, a nickel catalyst without rhenium can be used three times for liquid-phase hydrogenation, but it remains active during five operations if promoted with rhenium.

Hydrogenation of cotton-seed oil[95] on a Raney nickel–rhenium catalyst in absolute ethanol is 1.5–1.7 times faster than on a straight Raney nickel catalyst.

It was also shown[96,97] that the addition of 1–3% of rhenium to a nickel–aluminium alloy increases its activity towards the hydrogenation of cinnamic alcohol to phenylpropanol. If the rhenium content is increased to 5–7% the catalytic activity decreases, but in every case the rhenium-containing catalysts were more active than the nickel–aluminium alloy. The hydrogenation rate constant on a catalyst made from a 3% Re, 47% Ni, and 50% Al alloy was higher by a factor of 1.6 at 40° and a factor of 2 at 20° than the rate constant found in the hydrogenation of cinnamic alcohol on Raney nickel.

Rhenium–palladium alloy catalysts[98] have been studied in the hydrogenation of dimethylethynyl carbinol in water, 96% ethanol, 0.1*N* KOH in water and in ethanol, at 10, 20, 30, and 40°. Hydrogenation in water is produced by adsorbed hydrogen, but in ethanol the reaction involves hydrogen supplied from the bulk of the catalyst. The catalysts are stable both in aqueous and in alcoholic media, and show some selectivity when 0.1*N* KOH in 96% ethanol is used as the solvent. The reaction stops at the stage of half-hydrogenation. However, the palladium–rhenium catalyst is less active than the palladium–iridium alloy catalyst. The state of the surface during the reaction was monitored by potential measurements[99].

The activity of skeletal nickel–rhenium catalysts prepared from Ni–Re–Al alloys has been studied[100] in the hydrogenation of potassium maleate, potassium *o*-nitrophenate, and dimethylethynyl carbinol in 0.1*N* KOH solution, and of nitrobenzene in 50% ethanol. At temperatures below 40°, the skeletal nickel catalyst is deactivated towards the hydrogenation of compounds with multiple carbon–carbon bonds. At higher temperatures the rate of hydrogenation goes through a maximum as a function of rhenium concentration in the alloy. When potassium *o*-nitrophenate is reduced in 0.1*N* KOH, the reaction is drastically retarded as the rhenium content is increased, particularly at high temperatures. The rhenium was shown to increase the lattice parameter of the Raney nickel catalyst. The authors consider that the promoting effect of rhenium at elevated temperatures resides in its favourable influence on the activation of the  and –C≡C– bonds, and they ascribe the poisoning of the catalyst during the reduction of nitro compounds in alkaline media to oxidation of the rhenium or its hydride.

Mashkina and Vakurova[92] also demonstrated the promoting effect of rhenium. By adding 2.5% of rhenium to an industrial nickel–chromium catalyst, they obtained a much higher rate of hydrogenation (at 20° and under atmospheric pressure) of sulpholene to sulpholane:

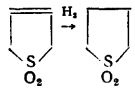


Table 6. Catalytic conversion of hydrocarbons on rhenium–palladium–alumina catalysts*.

Initial hydrocarbons	Contents in product wt.%						
	iso-C_6H_4						
	№ 1	№ 2	№ 1	№ 2	№ 1	№ 2	
	—	—	67.0	87.0			
	—	—	23.0	61.2			
n-C_6H_{14}	32.0	52.0					
	—	—					90

* No.1, 1% Pd, 1% Re, 98% Al_2O_3; No.2, 1% Pd, 1% Re, 98% Al_2O_3; H_2S: temperature 480°; pressure 10 atm; flow rate $v = 1.0\ h^{-1}$; H_2 to hydrocarbon ratio 5:1.

Ryashentseva and coworkers[101-104] studied the properties of mixed rhenium–palladium–alumina–silica catalysts towards the transformations of cyclohexane, methylcyclohexane, methylcyclopentane, and n-hexane[101,102]. The rhenium–palladium–alumina catalyst containing 1% of rhenium and 1% of palladium on fluorinated (0.4% F) alumina, and treated with hydrogen sulphide[102], was found to be the most active and stable towards the dehydrogenation of cyclohexane and methylcyclohexane, the dehydroisomerisation of methylcyclopentane, and the isomerisation of n-hexane. The results are summarised in Table 6. This catalyst was also used under reforming conditions on Baku B-70 light

petroleum and on the light petroleum fraction from the Volga-Urals oilfields. The results of these tests are given in Table 7.

Table 7. Properties of initial light petroleum fractions and of reforming products (470°, 10 atm, $v = 1.0\ h^{-1}$, H_2 : hydrocarbon = 5 : 1).

Properties	Initial fraction		Properties of product after 25 h operation of the catalyst		
			No.2 catalyst 1% Pd, 1% Re, Al_2O_3, H_2S		No.3 catalyst 1% Pd, Al_2O_3, H_2S
	Baku B-70	86–119°	B-70	86–119°	B-70
Refractive index n_D^{20}	1.4180	1.4040	1.4520	1.4260	1.4255
Specific gravity d_4^{20}	0.7529	0.7152	0.7928	0.7502	0.7545
Concentration of aromatic hydrocarbons, vol.%	5.5	6.0	57.0	38.0	20.5
Concentration of sulphur compounds, wt.%	0.0123	0.0116	0.009	0.010	0.008
	Engler distillation, °C				
Boiling begins	67.0	86.0	58.0	46.0	53.0
10%	88.5	91.0	87.0	75.0	80.0
50%	106.0	97.0	109.0	100.0	105.5
90%	156.0	107.0	161.0	140.0	151.0
Boiling ends	202.0	119.0	208.0	173.5	210.0

As Table 6 shows, the extent of dehydrogenation on a rhenium–palladium–alumina catalyst activated with hydrogen sulphide is 87% for cyclohexane and 90% for methylcyclohexane, and 61.2% of benzene can be obtained from methylcyclopentane. Catalysts consisting of rhenium (or palladium) alone on alumina gave much lower conversions of the hydrocarbons than the mixed catalyst. Reforming of Baku light petroleum and other fractions[75,102] on rhenium–palladium–alumina catalysts treated with hydrogen sulphide raised the aromatics content 7–10-fold, and lowered the concentration of sulphur compounds by a factor of 1.4. The addition of 1% of rhenium to a palladium–alumina catalyst treated with hydrogen sulphide increases the stability of the catalyst under reforming conditions by almost a factor of 4. As Table 6 shows, mixed rhenium–palladium–alumina are also active towards isomerisation reactions. Thus, the yield of hexane isomers on a rhenium–palladium–alumina catalyst is 32%, and 52% on a rhenium–palladium–alumina catalyst treated with hydrogen sulphide. Whereas a 1% rhenium–alumina gives only 7% isomerisation of n-hexane, the sulphided catalyst gives 14% isomerisation[101]. There was no indication of a decrease in the isomerisation activity of the mixed catalyst after prolonged operation (90 h). The activity of a catalyst containing 1% of palladium but no rhenium had fallen by a factor of 2 after 50 h. Hence, the addition of 1% of rhenium to a palladium–alumina catalyst increases the stability of the catalyst very significantly. All these findings point to the high efficiency of H_2S-treated rhenium–palladium–alumina catalysts for dehydrogenation, dehydroisomerisation, and isomerisation reactions.

This catalyst was tested under static and fluidised bed conditions for reforming the 72–102° fraction of Karadag light petroleum[104]. The results, set out in Table 8, show that the concentration of aromatic hydrocarbons in the reforming product is 36–42% after 25 h operation under static or fluidised bed conditions. The concentration of benzene increases 4-fold, that of toluene 5-fold. The concentration of C_5 and C_6 alkanes remains almost constant. In the initial light petroleum fraction, the hexane isomers account for ~50% of the total content of hexanes. Thus, the aromatic hydrocarbons are formed mainly by dehydrogenation of six-membered cyclanes, with a much smaller contribution from the dehydroisomerisation of alkylcyclopentanes. In subsequent studies of the stability of the catalyst it was shown that in a static layer the activity gradually decreases, and after 40 h the concentration of aromatic hydrocarbons in the reforming product has fallen to 20%, whereas under fluidised bed conditions the concentration of aromatics has barely decreased at all (36%) after 100 h operation. It follows that the stability of the catalyst is approximately 4 times higher for the fluidised bed than for the static catalyst. A likely explanation is that the macroscopic surface area of the catalyst is much higher in the fluidised bed than in the static layer, and also that isothermal conditions are more rigorously observed in the fluidised bed. After 100 h the catalyst was regenerated by air under atmospheric pressure at 400° (fluidised bed), and treated with hydrogen. The experiments were made under 10 atm pressure, at a flow rate of 1.5–2 changes per hour, and 10 : 1 ratio of H_2 to hydrocarbons. Under these conditions, the concentration of aromatics in the reforming product was increased 5-fold (as previously). Thus, we may conclude that the rhenium–palladium–alumina catalyst treated with hydrogen sulphide regains its full activity on being regenerated.

Table 8. Properties of initial 71–102° Karadag light petroleum and of reforming products under static and fluidised bed catalytic conditions (480°, flow rate 0.8–3.5 h^{-1}, 10 atm pressure, H_2 : hydrocarbon ratio 5–20).

Composition of petroleum and reforming products, wt.%	Initial 71–102° fraction	Static bed	Fluidised bed	
		Reforming products after operating catalyst for		
		25 h		100 h
Isopentane	1.4	1.2	1.1	0.9
n-Pentane	2.7	2.1	2.5	1.9
2,2-Dimethylbutane	0.3	0.4	0.7	0.5
2-Methylpentane + 2,3-dimethylbutane	5.9	6.3	6.2	5.8
3-Methylpentane	4.8	3.9	4.6	4.4
n-Hexane	12.4	10.9	11.6	10.3
n- and Isoheptane + dimethylcyclopentanes + methylcyclopentane	48.9	36.7	30.7	37.4
Methylcyclohexane	15.4	1.1	0.8	2.8
Benzene	3.7	15.1	18.7	12.9
Toluene	4.5	21.3	23.2	23.0

This work on the reforming of hydrocarbon mixtures on catalysts containing rhenium justifies the conclusion that this element offers interesting possibilities as a component of dehydrogenation, isomerisation, and dehydroisomerisation catalysts, offering enhanced activity and stability.

Müller and Schnabel[105] studied rhenium–platinum catalysts on carbon in the dehydrogenation of cyclohexane and the "C_5-dehydrocyclisation" of iso-octane at 250–400° under atmospheric pressure. Koppers coke [a brown coat coke (Ed. of Translation)] was found to be a better carrier than birch charcoal. The activity of the carbon-supported platinum–rhenium catalyst showed a significant improvement only when 50% of platinum and 50% of rhenium was used, and the platinum was deposited first. Otherwise, the activity of the Pt–Re catalysts, though much

higher than that of rhenium catalysts, was somewhat lower than the activity of platinum catalysts. A maximum activity is found at Pt or Re concentrations between 0 and 1 wt.%, followed by a sharp fall in catalytic activity. An increase in activity occurs at 5% Re content (or 2.5% Re and 2.5% Pt in mixed catalysts). The activity of the catalysts towards the dehydrocyclisation of iso-octane is very sensitive to the preparative conditions. Thus, catalysts prepared by impregnating the carbon with a platinum solution, with subsequent hydrogen reduction, are less active than catalysts in which the platinum was reduced by the Zelinskii formalin–alkali method. The advantage of using Koppers coke lies in the constancy of its composition.

However, there is no prospect as yet of using these catalysts in industrial production because no suitable method of regeneration has yet been found. Hence, only oxide carriers such as alumina, silica, alumina–silica, zeolite, etc., are likely to be of importance in petroleum refining applications of rhenium catalysts.

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We have shown that specific areas of application of rhenium in the field of catalysis can already be identified, despite the fact that the chemistry of the element began to be studied only recently (since the 1930's), and systematic studies of its catalytic properties are of even more recent date.

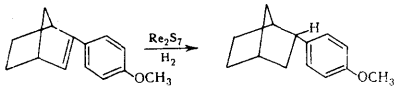
Rhenium catalysts can be of importance in the preparation of a number of rare organic compounds. For example, rhenium black[50] and $ReO.2H_2O$[55] are universal catalysts for the preparation of alcohols from ethanol to undecanol by reduction of the corresponding acids or ketones; the tetrahydropyran complex of Re_2O_7[52] and skeletal rhenium[56] are selective hydrogenation catalysts for the aromatic bond. The sulphides of rhenium have been found to have specific activity towards the dehydrogenation of alcohols to aldehydes and ketones[58,59], the reduction of the C=C double bond, the reduction of organosulphur compounds without cleavage of the C–S bond[59], of the azomethine group (C=N) without hydrogenation of the benzene or the thiophen ring[65,66], of carbonyl groups in aldehydes and ketones of the thiophen series[63,64], and the reductive alkylation of aromatic amines by ketones[67,69] without breaking the C–N bond or hydrogenating the ketone and the aromatic ring.

Lastly, addition of rhenium to hydrogenation catalysts[92,94-100] and reforming catalysts[101-104] produces a substantial improvement in the activity and stability of these catalysts. This observation may be important, and may lead to the practical use of rhenium catalysts in the chemical industry.

The recent paper by Davenport and coworkers[106], and our own very recent results, have had to be omitted from the present review.

Rhenium–alumina catalysts treated with hydrogen sulphide[107] are appreciably active in the dehydrocyclisation of diethyl sulphide to thiophen.

Rhenium heptasulphide reduces *p*-norbornenylanisole quantitatively to *endo*-norbornylanisole:



and also reduces the pyridine ring in substituted aryl-γ-pyridylmethanes and γ-arylpyridines.

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Zelinskii Institute of Organic Chemistry
USSR Academy of Sciences, Moscow