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Catalytic hydrogenation of thiolene 1,1-dioxides to thiolane 1,1-dioxide. Certain problems of the resistance of hydrogenation catalysts to sulfur

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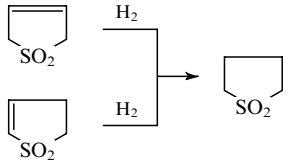
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Abstract. The state of research on the catalytic liquid-phase hydrogenation of 2- and 3-thiolene 1,1-dioxides to thiolane 1,1-dioxide is analysed. Data on the activities and selectivities of Group VIII metals and their complexes and sulfides, both massive and supported, as well as the reaction conditions and hydrogenation mechanisms are considered. The causes of the deactivation of catalysts in the synthesis of thiolane 1,1-dioxide and procedures for increasing their resistance to sulfur are described. Certain general problems of the resistance of hydrogenation catalysts to sulfur are discussed. The bibliography includes 130 references.

I. Introduction

Thiolane 1,1-dioxide, which has a series of valuable properties,[1] was first obtained in 1910 by the oxidation of thiolane.[2] However, a procedure proposed later [3–5] and based on the reduction of 2- and 3-thiolene 1,1-dioxides by hydrogen in the presence of catalysts proved to be more convenient.



The initial compounds for the synthesis of thiolane 1,1-dioxide are fairly readily available: the interaction of buta-1,3-diene with sulfur dioxide affords a 95 mol. % yield of 3-thiolene 1,1-dioxide and isomerisation of the latter in a basic medium leads to 2-thiolene 1,1-dioxide in up to 60 mol. % yield.[6]

Nowadays, thiolane 1,1-dioxide is widely used as a reaction medium, as a plasticising and stabilising additive, as a component of hydraulic liquids, and as an anticorrosion additive to oils. It is also employed to purify resins and plant oils, to prepare a sulfur emulsion in water, etc. It is particularly important to note the use of thiolane 1,1-dioxide as the extractant for the isolation of aromatic hydrocarbons from reformed petroleum products and as the solvent for the elimination of acid components from natural and industrial gases (see the relevant reviews [1, 7, 8]). The need for this product stimulated the development of studies on the catalytic hydrogenation of thiolene 1,1-dioxides and led to the initiation of industrial production.[7, 9]

Up to the 1960s, information about the hydrogenation of thiolene 1,1-dioxides and thiolane 1,1-dioxide could be found only in the patent literature and a few research communications. Analysis of the results published at that time showed [1] that traditional low-temperature hydrogenation catalysts, such as platinum (platinum black and dioxide), palladium (palladium black and Pd/C), or nickel (Raney nickel and Ni/SiO_2) may be used for the hydrogenation of 2- and 3-thiolene 1,1-dioxides and their substituted derivatives to the corresponding thiolane 1,1-dioxide. The hydrogenation is usually carried out at 20 – 40 °C and atmospheric or reduced pressure in ethanol, isopropyl alcohol, water, acetic acid, dioxane, benzene, or thiolane 1,1-dioxide. The complete reduction of unsubstituted thiolene 1,1-dioxide in the presence of an excess of the catalyst relative to the substrate (34 mass % – 250 mass %) requires several minutes, whereas in the presence of a low content of the catalyst (1 mass % – 4 mass %) up to 20 h is required.

Various investigators studied the hydrogenation of thiolene 1,1-dioxides under different conditions. In a number of instances, the catalytic activity was determined without testing for the presence or absence of diffusional complications and without taking into account the surface area of the active component, which greatly hinders comparison of the results. Extensive experimental data have now accumulated. Nevertheless, important factors such as the dependence of the activity of the metal on its surface concentration on various carriers, the mechanism and kinetics of the hydrogenation reaction, and the resistance of the catalysts to sulfur have not been considered in detail in the very brief reviews available.[10–14] It has therefore become necessary to analyse all the existing data and to determine the possible aspects of further research.

II. Hydrogenation of 2- and 3-thiolene 1,1-dioxides on massive and supported transition metal sulfides

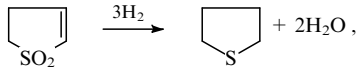
Group VI – VIII metal sulfides are used as catalysts in the hydrogenation reactions of sulfur-containing raw material. They are not poisoned by sulfur compounds and exhibit an adequate activity at elevated temperatures and pressures and for prolonged contact

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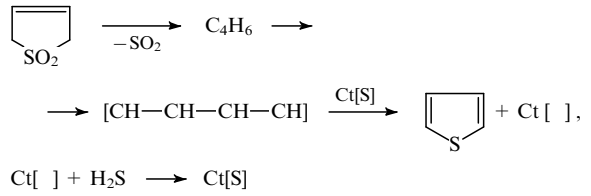
times.[15] Such severe conditions arise in the first place from the difficulty of activating hydrogen, which requires the transfer of its electrons to the acceptor centres, arising as a result of the displacement of electron density from the metal to the sulfur atom of the catalyst. The metal atoms in the sulfide are separated by sulfur atoms and this hinders the activation of unsaturated compounds which requires a structural correspondence.[16]

Molybdenum, tungsten, nickel, cobalt, and iron sulfides are not effective catalysts of the synthesis of thiolane 1,1-dioxide by the hydrogenation of thiolene 1,1-dioxides. Thus patent data (see the present author's earlier review[1]) indicate that the hydrogenation of 2-thiolene 1,1-dioxide on these sulfides proceeds with formation of thiolane:



while thiophene is formed from 3-thiolene 1,1-dioxide (250–425 °C, 2–20 MPa). In the latter case, the 3-thiolene 1,3-dioxide formed probably decomposes to buta-1,3-diene and sulfur dioxide. The reaction is known to proceed at a high rate at temperatures above 100 °C.[6] On metal sulfides at an elevated temperature, buta-1,3-diene is dehydrogenated with formation of the $-CH-CH-$ fragments, which interact with the catalyst sulfur atom to form thiophene. The loss of sulfur by the catalyst is made good by its interaction with the hydrogen sulfide formed on reduction of sulfur dioxide (Scheme 1):[17]

Scheme 1



Ct = catalyst.

It has been demonstrated experimentally [10–14, 18–22] that, at a lower temperature in the presence of certain transition metal sulfides, thiolene 1,1-dioxides are reduced to thiolane 1,1-dioxides (Table 1). The hydrogenation is carried out in the liquid phase in the presence of both massive and supported catalysts. The degree of conversion of the substrate, the yield of thiolane 1,1-dioxide, the selectivity (S), and the rate of formation of the dioxide (W), as well as the stability of the catalyst depend on the reaction conditions, namely on the nature of the solvent, temperature, hydrogen pressure (P), contact time (t), the initial thiolene 1,1-dioxide concentration (c), and the content of the catalyst in solution (g_{ct}).†

It follows from Table 1 that, in the hydrogenation of 3-thiolene 1,1-dioxide, dissolved in isopropyl alcohol, at an elevated temperature and pressure in the presence of γ-Al_2O_3 modified with 0.5 mass % of osmium, platinum, rhenium, or rhodium sulfides or 2.4 mass % of palladium sulfide, and also in the presence of the 5% RuS_2/SiO_2 catalyst, the yield of thiolane 1,1-dioxide does not exceed 1 mol. % with $S \leqslant 10\%$ and $W = 0.008-0.025$ mmol h^{-1} g^{-1}. On the catalyst obtained by depositing 20 mass % of Re_2S_7 on γ-Al_2O_3, the rate of reaction increases by an order of magnitude ($W = 0.25$ mmol h^{-1} g^{-1}) and the yield of thiolane 1,1-dioxide is 10% for $S = 14\%$. When massive Re_2S_7 is used, the yield reaches more than 50% and $W = 1.3$ mmol h^{-1} g^{-1}. The unsatisfactory results can be explained by the decomposition of the unstable initial substrate under the conditions of a high temperature (100 °C) and a long contact time (7 h). Indeed, when the contact time is reduced to 1–2 h the hydrogenation of 3-thiolene 1,1-dioxide on the 2.5% PdS/Al_2O_3 catalyst in dilute solutions in methanol, butanol, and dimethylformamide leads to the formation of thiolane 1,1-dioxide in 50%–90% yield with $W = 0.42-0.85$ mmol h^{-1} g^{-1} and $S \leqslant 90\%$ (100 °C, $P = 5$ MPa, $c = 0.04$ M, $g_{ct} = 50$ g $litre^{-1}$).

A decrease in temperature to 20 °C induces a rise of the selectivity in the formation of thiolane 1,1-dioxide. Thus, in the hydrogenation of 3-thiolene 1,1-dioxide on massive platinum, palladium, or rhodium sulfides at $P = 5$ MPa, the product yield is only 2%–5%, but $S = 100\%$ and $W = 21-62$ mmol $h^{-1}g^{-1}$.[18] Under these conditions, the activity of rhodium sulfide calculated per gram of the massive catalyst is twice as high as that of palladium sulfide and three times as high as that of platinum sulfide (Table 1). The specific activities, calculated per unit area, of rhodium and palladium sulfides are approximately the same and exceed by more than an order of magnitude the specific activity of platinum sulfide (6.84, 5.13, and 0.32 mmol h^{-1} m^{-2} respectively).

Table 1. Hydrogenation of 2- and 3-thiolene 1,1-dioxides on metal sulfides in isopropyl alcohol ($c = 0.25-0.4$ M, $g_{ct} = 10$ g $litre^{-1}$).[18, 19]

Catalyst[a]	T/°C	P/MPa	t/min	Yield of thiolane 1,1-dioxide (%)	S (%)	W[b]
3-Thiolene 1,1-dioxide						
Rh_2S_3 (9)	20	5	1	5	100	61.6
0.5% Rh_2S_3/Al_2O_3	100	25	420	1	10	0.025
PdS (6)	20	5	0.8	2.5	100	30.8
2.4% PdS/Al_2O_3	100	25	420	1	1	0.017
PtS_2 (66)	20	5	1	2	100	20.8
0.5% PtS_2/Al_2O_3	100	25	420	0.5	0.5	0.008
Re_2S_7 (9)	100	25	420	51	52	1.3
0.5% Re_2S_7/Al_2O_3	100	25	420	0.5	1	0.02
20% Re_2S_7/Al_2O_3	100	25	420	10	14	0.25
5% RuS_2/SiO_2	100	25	420	0.5	0.5	0.008
0.5% OsS_2/Al_2O_3	100	25	420	1	1	0.025
2-Thiolene 1,1-dioxide						
Rh_2S_3 (9)	150	11	60	90	90	22.5
0.5% Rh_2S_3/Al_2O_3	100	25	180	11	18	0.92
	150	25	180	28	28	2.33
PdS (6)	150	11	30	68	100	34.1
	150	11	60	84	88	21.0
0.5% PdS/Al_2O_3	150	25	180	77	77	6.4
2.4% PdS/Al_2O_3	150	25	180	68	68	5.7
4.7% PdS/Al_2O_3	150	11	60	30	100	7.5
Re_2S_7 (9)	150	11	60	48	72	12.0
0.5% Re_2S_7/Al_2O_3	150	25	180	67	67	0.02
20% Re_2S_7/Al_2O_3	100	25	420	49	50	1.8
PtS_2 (66)	150	16	60	47	68	11.7
0.5% PtS_2/Al_2O_3	100	25	420	9	10	0.22
OsS_2 (34)	150	11	60	78	88	19.6
0.5% OsS_2/Al_2O_3	150	25	180	7	10	0.6
5% RuS_2/SiO_2	100	25	420	16	34	0.42
WS_2 (11)	150	11	60	6	39	1.5
NiS (19)	150	11	60	3	46	0.83
CoS (9.5)	150	11	60	6	86	1.5

[a] The values of S_{sp} expressed in m^2 g^{-1} are given in brackets. [b] Expressed in mmol h^{-1} g^{-1}.

† All the data presented below are expressed in identical units: the rate of reaction is expressed in moles of thiolane 1,1-dioxide formed per unit time on 1 g of the catalyst, on 1 g-atom of the metal, or on 1 m^2 of the surface of the active component; the stability of the catalyst is expressed in millimoles of thiolane 1,1-dioxide obtained during the period of the complete deactivation of 1 g of the catalyst or 1 m^2 of the metal; the content of the substrate in the solution hydrogenated is expressed on the molar scale and that of the catalyst in g $litre^{-1}$.

In the hydrogenation of the thermally more stable 2-thiolene 1,1-dioxide on transition metal sulfides, satisfactory parameters likewise cannot be always attained.[19,20] Thus in isopropyl alcohol the hydrogenation does not take place on massive V_2S_3 ($S = 7\,m^2\,g^{-1}$) and MnS ($S_{sp} = 2.3\,m^2\,g^{-1}$), whereas on tungsten, nickel, and cobalt sulfides the yield of thiolane 1,1-dioxide does not exceed 6% for a reaction rate of 1.5 mmol h^{-1} g^{-1}. When massive rhenium, platinum, osmium, rhodium, or palladium sulfides are used as the catalyst, the yield of thiolane 1,1-dioxide reaches 50% – 90% in 1 h, the selectivity is less than 100% owing to the partial decomposition of the substrate, and the rate of hydrogenation per gram of the catalyst exceeds by an order of magnitude the rate of reaction on tungsten, nickel, and cobalt sulfides ($W = 12-23$ mmol h^{-1} g^{-1}). However W decreases when the sulfides are deposited on Al_2O_3 or SiO_2 (100 – 150 °C, $P = 11-25$ MPa, $c = 0.2-0.37$ M) (Table 1).

In terms of their specific activity in the hydrogenation of 2-thiolene 1,1-dioxide at 150 °C at $P = 11$ MPa, the massive metal sulfides can be arranged in the following series (the values of W expressed in mmol h^{-1} m^{-2} are given in brackets):

$$PdS\ (3.5) > Rh_2S_3\ (2.5) > Re_2S_7\ (1.3) > OsS_2\ (0.58) > > PtS_2\ (0.18) > CoS\ (0.16) > WS_2\ (0.14) > NiS\ (0.0044).$$

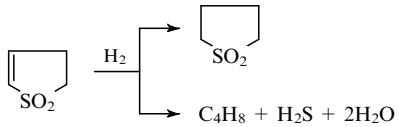
Nickel sulfide has the lowest specific activity, while platinum, rhenium, cobalt, and tungsten sulfides are approximately four times more active and rhodium and palladium sulfides are up to 60 – 80 times more active than nickel sulfide. Under the same conditions, the greatest selectivity in the formation of thiolane 1,1-dioxide is obtained on massive rhodium, palladium, osmium, and cobalt sulfides ($S \approx 90\%$). It is somewhat lower on rhenium and platinum sulfides ($S \approx 70\%$), and is especially low on tungsten and nickel sulfides ($S < 50\%$).

The hydrogenation of 2-thiolene 1,1-dioxide has been investigated in greater detail on palladium sulfide, 0.5 mass % – 7.6 mass % of which had been deposited on γ-Al_2O_3.[11,19]

In the presence of 0.5% PdS/Al_2O_3, an increase in temperature from 50 to 200 °C with the remaining parameters unaltered leads to an increase in the yield of thiolane 1,1-dioxide from 14% to 70% for $S = 70\%$ ($P = 25$ MPa, $c = 0.26$ M, $g_{ct} = 10$ g litre^{-1}, $t = 7$ h). On the 4.7% PdS/Al_2O_3 catalyst, such an increase in temperature induces an increase in yield from 5% to 36% for $S = 100\%$ ($P = 11$ MPa, $c = 0.21$ M, $g_{ct} = 10$ g litre^{-1}, $t = 1$ h).

On the 2.4% PdS/Al_2O_3 catalyst at 150 °C, $P = 25$ MPa, and $g_{ct} = 10$ g litre^{-1}, the degree of conversion of 2-thiolene 1,1-dioxide is independent of its initial concentration in the range from 0.02 to 0.12 M, while the rate of hydrogenation is proportional to the concentration of the substrate. The rate of reaction at $c = 0.37$ M is proportional to the hydrogen pressure in the range from 1 to 15 MPa. For higher values of c and P, the rate ceases to change, *i.e.* the reaction is of zero order with respect to 2-thiolene 1,1-dioxide and hydrogen.

On the 2.4% PdS/Al_2O_3 catalyst, the degree of conversion of 2-thiolene 1,1-dioxide dissolved in isopropyl alcohol may attain 100%, but the yield of thiolane 1,1-dioxide does not then exceed 70% (150 °C, $P = 25$ MPa, $c = 0.37$ M, $g_{ct} = 10$ g litre^{-1}), since hydrogenolysis products are formed together with thiolane 1,1-dioxide. The degree of conversion does not affect the selectivity. On the basis of these data, it was concluded[19] that the initial 2-thiolene 1,1-dioxide, and not its hydrogenation product, undergoes hydrogenolysis, *i.e.* the hydrogenation and hydrogenolysis reactions proceed independently.



The PdS/Al_2O_3 catalyst is stable under the conditions of the hydrogenation of 2-thiolene 1,1-dioxides even after the formation of ~415 mmol of thiolane 1,1-dioxide on 1 g of the catalyst, the rate of reaction remains unchanged.

III. The activities and stabilities of metal complexes in the hydrogenation reactions of 2- and 3-thiolene 1,1-dioxides

Metal complexes are promising catalysts for the reduction of various unsaturated compounds.[23] Certain platinum, palladium, and rhodium complexes exhibit an enhanced resistance to sulfur.[24–29] The use of Group VIII metal complexes for the hydrogenation of 2- and 3-thiolene 1,1-dioxides has so far been investigated in insufficient detail.

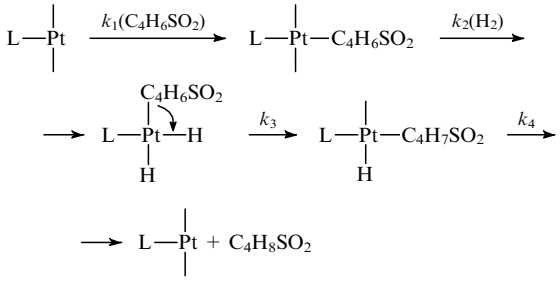
Rhodium complexes. In the hydrogenation of 3-thiolene 1,1-dioxide in the presence of tris(*tert*-phosphine)- or tris(*tert*-arsine)-rhodium nitrosyl complexes, a quantitative yield of thiolane 1,1-dioxide is attained after 16 h at 56 °C and $P = 4$ MPa.[30]

Nickel complexes. In the presence of nickel acetylacetonate in solution in benzene to which aluminium isobutoxide has been added at a concentration of 31.6 M, exhaustive hydrogenation of 3-thiolene 1,1-dioxide takes place (25 °C, $P = 1.4$ MPa, $c = 1.8$ M, $g_{ct} = 5.3$ mmol litre^{-1}, $t = 35$ min).[31] The rate of formation of thiolane 1,1-dioxide per gram-atom of nickel is 576 mol h^{-1}.

Platinum complexes. In the presence of the complex $PtCl_2(H_2O)[P(C_6F_5)_3]$ reduced by hydrogen, 3-thiolene 1,1-dioxide, dissolved in butanol, is hydrogenated to thiolane 1,1-dioxide in a yield of about 100%.[32] The isomerisation of the initial substrate to 2-thiolene 1,1-dioxide also takes place to a slight extent (0.5%) (25 °C, $P = 0.1$ MPa, $c = 0.12$ M, concentration of the complex 0.01 M, $t = 1.5$ h). The rate of hydrogenation is 11.4 mol h^{-1} (g-atom Pt)$^{-1}$. A kinetic study showed[33] that the order of this reaction with respect to platinum at a platinum concentration in the range $[Pt] = (2.5-10) \times 10^{-3}$ M is unity. Hence it was concluded that the catalyst contains no ligands capable of splitting off from the initial complex under the influence of the solvent. The rate of hydrogenation at $c < 0.01$ M increases with increase in the 3-thiolene 1,1-dioxide concentration raised to a power of 0.55, whilst at $c = 0.05-0.1$ M it remains unchanged. The order of the reaction with respect to hydrogen at pressures close to atmospheric is zero, whilst at low partial pressures (~0.006 MPa) it increases to 0.7. In the temperature range from 0 to 62.5 °C, the activation energy for the reaction is 46 kJ mol^{-1}.

It has been suggested[33] that the reaction proceeds *via* consecutive stages involving coordination to the complex of 3-thiolene 1,1-dioxide and hydrogen and the formation of a hydride complex and its decomposition (Scheme 2).

Scheme 2



Here L is the stabilising ligand in the reduced platinum complex formed from $P(C_6F_5)_3$, while $k_1 - k_4$ are the rate constants for the corresponding stages. The rate of reaction is limited by the formation of the hydride complex (stage 3) and is described by the equation

$$W = \frac{k_3 K_1 K_2 c_1 c_2 c_3}{1 + K_1 c_2 + K_1 K_2 c_2 c_3},$$

where K_1 and K_2 are the equilibrium constants of stages 1 and 2, c_1 is the overall concentration of the complexes formed in all the reaction stages, c_2 is the concentration of 3-thiolene 1,1-dioxide, and c_3 is the concentration of hydrogen in solution, equal to P_{H_2} multiplied by the solubility coefficient of the gas.

At a high substrate concentration, the equation becomes

$$W = \frac{k_3 K_2 c_1 c_3}{1 + k_2 c_3},$$

and at a high hydrogen concentration it assumes the form

$$W = k_3 c_1 .$$

These equations agree with experimental data.

On consecutive hydrogenation of several portions of 3-thiolene 1,1-dioxide in the same contact solution, the reaction rate diminishes from experiment to experiment After the formation of 100 mmol of thiolane 1,1-dioxide per mg-atom of platinum, the initial activity becomes smaller by a factor of two. It can also be postulated that the deactivation of the platinum complex is associated with the formation of small amounts of buta-1,3-diene and sulfur dioxide on decomposition of the substrate. However, the addition of buta-1,3-diene at a concentration of $(3.3-16.7)\times10^{-3}$ M did not decrease but actually increased the activity of the catalyst by a factor of 1.3–3. On the other hand, sulfur dioxide is a poison for the platinum complex, its introduction into the solution hydrogenated at a concentration of 1.2×10^{-3} M (molar ratio SO_2 : Pt = 0.1) reduces the initial activity of the catalyst approximately by a factor of 80. In the presence of the above platinum complex, SO_2 is not reduced to hydrogen sulfide even after 3.5 h and it was therefore concluded [32] that the poison for the catalyst considered is sulfur dioxide itself.

Homogeneous palladium complexes. The hydrogenation of 2-thiolene 1,1-dioxide has been investigated [34] in the presence of palladium complexes with sulfur- and nitrogen-containing ligands in solution in dimethyl sulfoxide. The potassium tetrahydroborate-reduced palladium complexes of dimethyl sulfide and dimethyl sulfoxide, $PdCl_2\cdot(DMS)_2\cdot KBH_4$ and $PdCl_2\,(DMSO)_2\cdot KBH_4$, in which the degree of oxidation of palladium is reduced, accelerate the hydrogenation of 2-thiolene 1,1-dioxide. The reaction proceeds at a high rate W = 1 mol min^{-1} (g-atom Pd)$^{-1}$ (20 °C, P = 0.1 MPa, c = 0.127 M). The analogous palladium complexes of diethyl sulfide or thiolane are less active [W = 0.06 and 0.03 mol min^{-1} (g-atom Pd)$^{-1}$ respectively] and decompose under the influence of the reaction medium with liberation of metallic palladium.

The homogeneous palladium complex of dimethylformamide ($PdCl_2\cdot DMF$) proved to be approximately 45 times more active than the complexes with sulfur-containing ligands.

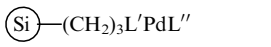
However, the addition of divalent sulfur compounds reduces the initial activity of the homogeneous palladium complexes. Thus, when thiophene or thiolane were added to the hydrogenated solution at a concentration of 50×10^{-3} M, the activity of the palladium complex of dimethyl sulfide diminished by a factor of 2 and the complex decomposed with liberation of metallic palladium. In order to poison the palladium complex of dimethyl sulfoxide to the same extent, it is necessary to introduce ten times more of thiolane to the hydrogenated solution. This can be accounted for by the difficulty of the incorporation of thiolane in the coordination sphere of the palladium complex, since palladium forms bonds with the sulfur and oxygen atoms of dimethyl sulfoxide.

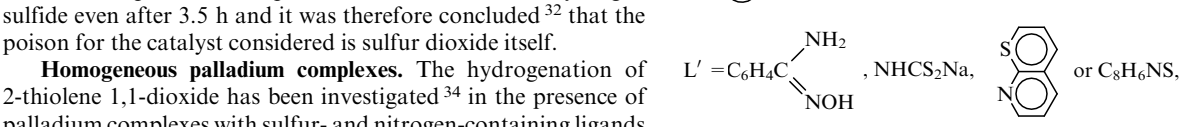
The activity of the complex $PdCl_2\cdot DMF$ diminishes by a factor of 2 after the introduction into the solution of thiophene at a concentration of 60×10^{-3} M or thiolane at a concentration of 0.3×10^{-3} M. Such a high difference between the toxicities can be accounted for by the fact that dimethylformamide, which is a stronger electron donor, can compete with thiophene for coordination to palladium, whereas thiolane substitutes dimethylformamide in the coordination sphere of palladium, forming a complex with the latter. The complex is unstable in a reducing medium and decomposes to metallic palladium, which is readily deactivated (see Section V). In terms of resistance to poisoning by thiolane, $PdCl_2\cdot DMF$ is inferior to palladium complexes with sulfur-containing ligands by 2–3 orders of magnitude.

The cause of the deactivation of homogeneous palladium complexes has been investigated [34] by UV and NMR spectroscopy. Absorption bands characteristic of the Pd^{2+}–S bond (26 000 and 34 000 cm) appear in the UV spectrum of the complex partly deactivated by the addition of $(5-10)\times10^{-3}$ M thiolane (poison : Pd = 2–5). At a thiolane concentration of 50×10^{-3} M (poison : Pd = 50), all the absorption bands vanish from the spectrum, which indicates the decomposition of the complex.

The ^{13}C NMR spectra of a $PdCl_2\cdot(DMS)_2\cdot KBH_4$ specimen to which small amounts of thiolane have been added exhibit signals belonging to thiolane coordinated to palladium (δ = 40.3 and 32.8 ppm) and to free dimethyl sulfide (δ = 20.6 ppm). On this basis, it was concluded that deactivation occurs as a result of the displacement by thiolane of the initial ligand from the coordination sphere of the complex and the disruption of the initial structure of the latter In hydrogen, the newly formed complex decomposes with liberation of metallic palladium, which is readily poisoned by sulfur compounds.

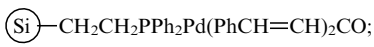
Heterogenised palladium complexes. The hydrogenation of 2- and 3-thiolene 1,1-dioxides on mononuclear and polynuclear Pd^{2+} and Pd^0 complexes immobilised on silicon dioxide has been investigated.[34–38] These complexes include the mononuclear Pd^{2+} complexes



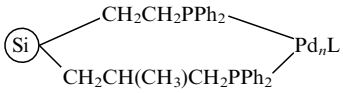


L″ = Cl, OAc, OH;

the mononuclear Pd^0 complex

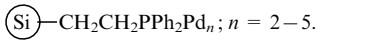


and polynuclear complexes of the type



L = OAc, Cl; n = 2–6

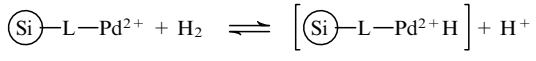
or



In the presence of heterogenised complexes in methanol and isopropyl alcohol, thiolene 1,1-dioxides are fully reduced to thiolane 1,1-dioxide (20 °C, P = 0.1 MPa, c = 0.127 M, g_{ct} = 1.5–10 g $litre^{-1}$). Depending on the composition of the complex, the rate of hydrogenation ranges from 1 to 90 mol min^{-1} (g-atom Pd)$^{-1}$ (Refs 35, 36), *i.e.* has the same order of magnitude as on the homogeneous complex $PdCl_2\cdot DMF$ and on supported metallic palladium (0.2 mass % – 5 mass %).[34]

The catalytic activity of mononuclear Pd^{2+} complexes increases with increase in the instability constant of the complex.[35] The hydrogenation reaction must involve the coordination of thiolene 1,1-dioxide with formation of a π-complex and the activation of hydrogen *via* the formation of palladium hydride. Palladium hydride is formed on the Pd^{2+} complex on transfer of electron density from hydrogen to palladium.[29] It has been suggested [37,38] that the rate-limiting stage of the hydrogenation of thiolene 1,1-dioxide on Pd^{2+} complexes is the activation of hydrogen. After the enhancement of the electron-donating prop-

erties of the ligands, the instability constant decreases. This shifts the equilibrium



towards a decrease in the concentration of palladium hydride and hence leads to a decrease in the rate of hydrogenation.

Polynuclear diphosphine Pd^0 complexes, immobilised on silicon dioxide, are somewhat less active than the mononuclear complexes. Their activity increases with increase in the number of palladium atoms from 2 to 6. The monophosphine Pd^0 complex is the most active. The rate of reaction on this complex reaches 92 mol min^{-1} (mol Pd)$^{-1}$, which can be accounted for by its conversion under the hydrogenation conditions into the coordinatively unsaturated immobilised complex $(Si)-(CH_2)_2PPh_2Pd^0$, which activates hydrogen and multiple bonds more readily.[29]

In the course of one experiment, the activity of the heterogenised complex does not change, but, after prolonged hydrogenation of 2- and 3-thiolene 1,1-dioxides, a slow deactivation of the catalyst is observed. It is probably caused by the effect of the divalent and tetravalent sulfur compounds formed. The resistance of the complexes to sulfur was determined by adding thiolane and thiophene to the hydrogenated solution.[34–38] It was found that the resistances of the mononuclear Pd^{2+} and polynuclear Pd^0 complexes to poisoning by the above substances are approximately the same. The immobilised palladium complexes with nitrogen-containing ligands are 40–500 times less resistant to poisoning by thiolane and thiophene than the homogeneous palladium complex of dimethylformamide.[34]

The causes of the deactivation of the heterogenised palladium complexes by thiolane and thiophene have been investigated.[13,34–38] Thiolane is a stronger poison than thiophene adsorption measurements have shown that the formation constant of the thiophene–catalyst complex is three times smaller than the corresponding constant for the thiolane–catalyst complex. It follows from desorption experiments that the deactivation by thiophene is partly reversible, whilst thiolane poisons the complex irreversibly. In dimethylformamide, which is an effective complex-forming agent and competes with the sulfur-containing poison, the resistance of the complex to poisoning is greater than in isopropyl alcohol (for the ratio poison : Pd = 100 : 1). The stability of the mononuclear Pd^{2+} complexes depends on the electron-donating capacity of the inner ligands, characterised by the instability constant of the complex with decrease in the latter, the strength of the $(Si)-L-Pd$ linkage increases, while the ability of palladium to be coordinated to the poison ($(Si)-L-Pd\leftarrow S<$) diminishes. The stability of the polynuclear complexes is determined both by the strength of the bond between palladium and the inner ligand and by steric factors. The role of the latter increases with increase in nuclearity. Owing to the small size of the framework of the cluster, not all the palladium atoms are sterically capable of forming bonds with the molecules of the poison, but they can activate hydrogen.

According to XPES data, the mononuclear Pd^{2+} complexes change after treatment with thiolane In the Pd3*d* spectral range, the binding energy diminishes from 337.2 to 336.7 eV for $B = 3.4–3.5$ eV, which indicates a decrease in the valence of palladium. The intensity of the Pd3*d*/Si3*p* lines then decreases slightly (from 0.23 to 0.21). In the region of S2*p* and S2*s*, sulfur lines were observed. A shoulder appears in the UV spectrum of the specimen treated with the poison in the range 34 000–24 000 cm^{-1}, which corresponds to the bond between Pd^{2+} and sulfur. The XPES spectra of the initial Pd^0 complex and the same complex treated with thiolane are characterised by a constant binding energy (336.1 eV) and line half-width (4.4–4.1 eV). The decrease after the treatment of the catalyst in the intensity of the Pd3*d*/Si2*p* lines from 0.36 to 0.26 can be explained by the shielding of the palladium signal by the adsorbed molecules of the poison.

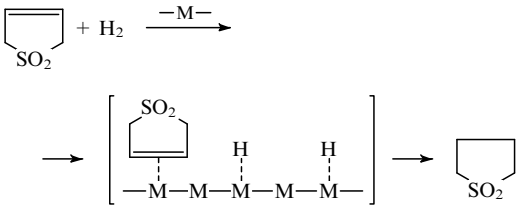
Analysis of the UV spectra also indicates the preservation of the structure of the complex when it is treated with thiolane (absorption bands at 28 000, 22 000, and 16 000 cm^{-1}). Treatment with a large amount of the poison at an elevated temperature induces the decomposition of the initial structure of the complex, which is indicated by the decrease in the binding energy, the line half-width, and the intensity of the signals in the XPES spectrum and also by the disappearance from the UV spectrum of the bands characteristic of the initial complex. It may be that the decomposition of the complex is accompanied by the formation of the $Pd\leftarrow :S<$ bond. Thus the deactivation of the palladium complexes immobilised on silicon dioxide takes place as a consequence of the displacement of the outer ligand by the sulfur poison entering into the coordination sphere of palladium and of the formation of a bond between palladium and sulfur. Under certain conditions, the structure of the complex is fully disintegrated.

IV. The activities of massive and supported metals in the hydrogenation reactions of thiolene 1,1-dioxides

Group VIII metals are used widely for the low-temperature hydrogenation of various unsaturated organic compounds.[17,39]

The multiple bond in thiolene 1,1-dioxides is activated by virtue of the presence of the electron-accepting sulfonyl group.[6,40] This facilitates the formation of a complex with participation of the C=C bond, which may become saturated in the presence of activated hydrogen in the system (Scheme 3).

Scheme 3



The reaction mechanism involves the postulate that the unsaturated organic substrate and hydrogen are activated on different active centres as a result of the transfer of electron density from the occupied atomic orbital of the metal to the C=C bond and to the unoccupied antibonding molecular orbitals of hydrogen.[17,39,41] This is to some extent confirmed, particularly by the results of experiments involving the introduction into the reaction mixtures of additives competing with the reactants for the formation of bonds with the metal. Thus, in the interaction of sulfur dioxide — a strong electron acceptor[40] — with the metal, electrons are transferred to the *d* orbital of the sulfur atom and this prevents the formation of a π-olefin complex by the metal. Hydrogen sulfide forms a coordinate bond as a result of the transfer of the lone pair of sulfur to the unoccupied orbital of the metal, which ultimately leads to the formation of a surface metal sulfide, which poorly activates hydrogen.[15]

It has been shown in a series of studies that 2- and 3-thiolene 1,1-dioxides are hydrogenated on Group VIII metals under mild conditions to thiolane 1,1-dioxide with 100% selectivity.[10–14,42] More studies have been devoted to the reaction involving 3-thiolene 1,1-dioxide than to the reaction in which 2-thiolene 1,1-dioxide is hydrogenated because of the relative availabilities of the two dioxides. However, 3-thiolene 1,1-dioxide readily dissociates to buta-1,3-diene and sulfur dioxide. Its vigorous decomposition begins above 100 °C, but it decomposes partly even at room temperature. 3-Thiolene 1,1-dioxide therefore always contains a certain amount of sulfur dioxide, which has a definite effect on the catalytic properties of metals. 2-Thiolene 1,1-dioxide is free of this disadvantage because it is thermally more stable.[6]

The hydrogenation of thiolene 1,1-dioxides on Group VIII metals is carried out in solutions at a low temperature and atmospheric or elevated pressure. The liquid-phase hydrogenation of 3-thiolene 1,1-dioxide has been studied in greatest detail on

metallic rhodium, nickel, and palladium, and in much smaller detail on osmium, iridium, ruthenium, and platinum. The results obtained on hydrogenation of thiolene 1,1-dioxides in the presence of Group VIII metals are examined below.

Iridium and osmium. The hydrogenation of 3-thiolene 1,1-dioxide on iridium and osmium has been investigated at 20 °C and $P = 5$ MPa in isopropyl alcohol to which 10 mass % of thiolane 1,1-dioxide had been added (Table 2).[42] In the presence of iridium black, exhaustive reduction of 3-thiolene 1,1-dioxide took place in 5 min {$g_{ct} = 10.7$ g litre^{-1}, $[SO_2] < 0.03 \times 10^{-3}$ M}. The initial rate of reaction in the kinetic region (for 20% conversion) was 0.39 mol h^{-1} g^{-1}. Iridium, deposited in an amount of 1 mass % – 2 mass % on γ-Al_2O_3, exhibited a somewhat higher activity than iridium black ($W = 0.5$ mol h^{-1} g^{-1}). It may be that the degree of dispersion of iridium in the supported catalyst is somewhat greater, since the rate constant on the supported metal, referred to its unit surface, agrees with the value found for iridium black.

The 1.8 mass % Os/γ-Al_2O_3 catalyst has a lower activity than the iridium catalyst; for $g_{ct} = 21.5$ g litre^{-1}, complete reduction of 3-thiolene 1,1-dioxide is attained after 30 min ($W = 0.04$ mol h^{-1} g^{-1}).

Table 2. The activities and stabilities of osmium, iridium, ruthenium, and platinum catalysts in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, $P = 5$ MPa, $c = 0.4$ M, solvent — isopropyl alcohol to which 10% of thiolane 1,1-dioxide has been added).[42]

Catalyst	S_{sp} [a] /m^2 g^{-1}	Activity [b]		Stability	
		see [c]	see [d]	mmol g^{-1}	mmol m^{-2}
1.8% Os/Al_2O_3	–	0.8	–	8.3	–
Ir	4	8.3	2.1	28	6.7
1% Ir/Al_2O_3	200	5.6	2.8	17	8.3
1.9% Ir/Al_2O_3	210	11.2	2.8	33	8.3
Ru	8	8.3	1.0	24	3.3
1% Ru/Al_2O_3	250	2.5	1.0	8	4.2
2% Ru/Al_2O_3	200	4.4	1.1	15	3.3
Pt	2.2	44	19	44	20
	88	1377	18	–	–
0.6% Pt/Al_2O_3	267	29	18	33	21
2% Pt/Al_2O_3	100	32	17	33	17

[a] Specific surface calculated per unit mass of the metal. [b] The activity given in this and subsequent tables represents the rate constant. It was determined to within ± 10 rel. % per unit surface of the metal. [c] Expressed in mol h^{-1} g^{-1}. [d] Expressed in mol h^{-1} m^{-2}.

The rate of hydrogenation on iridium is proportional to the concentration of 3-thiolene 1,1-dioxide (at $c = 0.07 – 0.6$ M) and the hydrogen pressure (at $P = 0.1 – 2$ MPa). In the range of higher values of the above parameters, the rate of reaction remains unchanged.

Ruthenium. The activity of ruthenium in the hydrogenation of 3-thiolene 1,1-dioxide is close to that of iridium (Table 2). On ruthenium black, the 100% yield of thiolane 1,1-dioxide is attained after 6 min at the reaction rate in the kinetic region $W = 0.4$ mol h^{-1} g^{-1} {$c = 0.36$ M, $g_{ct} = 10.7$ g litre^{-1}, $[SO_2] < 0.03 \times 10^{-3}$ M}.[42] Under the same conditions, the rate of hydrogenation on supported ruthenium (1 mass % – 2 mass % of Ru on γ-Al_2O_3) is 0.1 – 0.2 mol h^{-1} g^{-1}. The specific activities of ruthenium on a carrier and of ruthenium black are the same (Table 2). However, if the hydrogenation of 3-thiolene 1,1-dioxide takes place under the conditions of diffusional complications (large catalyst grains, inadequate stirring of the mixture), the supported ruthenium catalyst exhibits a reduced activity:[43] exhaustive hydrogenation of 3-thiolene 1,1-dioxide in isopropyl alcohol is attained on this catalyst only after 0.5 – 1 h {20 °C, $P = 0.1 – 10$ MPa, $c = 0.2$ M, $g_{ct} = 9 – 18$ g litre^{-1}, $[SO_2] < 0.03 \times 10^{-3}$ M}.

The activity of supported catalysts can be influenced by the chemical composition of the initial ruthenium compounds, which were potassium ruthenate and ruthenium chloride subjected to successive reduction with hydrogen at 300 °C. At atmospheric pressure, the activity of the catalyst prepared by depositing on charcoal the ruthenium obtained from potassiun ruthenate was higher than the activity of the catalyst obtained from ruthenium trichloride. On the other hand, the aluminoruthenium catalysts obtained from potassium ruthenate and ruthenium trichloride have approximately the same activities. The catalyst on silicon dioxide, obtained by depositing ruthenium obtained from the trichloride, is appreciably more active than the specimen prepared from potassium ruthenate.

When the same initial ruthenium compound is used, the catalytic activity is influenced by the nature of the carrier. Thus the activities of the catalyst on γ-Al_2O_3 and activated charcoal are an order of magnitude higher than the activity of ruthenium on silicon dioxide. It has been suggested[43] that this is caused by the different degrees of dispersion of ruthenium and the different chemical compositions of the active component, which consists of a mixture of metallic ruthenium and its oxide, the activities of which differ by a factor of 2.[42]

When 5 mass % of ruthenium is deposited on the Ni/Cr_2O_3 or Ni/SiO_2 industrial nickel catalyst, the activity of the latter either does not change or decreases. On the other hand, the introduction of 5 mass % of ruthenium (obtained from ruthenium trichloride) into an industrial aluminoplatinum catalyst increases its activity by a factor of 2.[43]

A kinetic study showed[42] that at $P < 2$ MPa the rate of hydrogenation is proportional to the hydrogen pressure and is independent of the concentration of the substrate. The process is apparently limited by the activation of hydrogen. When 3-thiolene 1,1-dioxide is introduced into a hydrogenated solution containing the hydrogen-saturated 5% Ru/Al_2O_3 catalyst, the potential undergoes a very marked shift to the anodic region (by 600 – 700 mV), which indicates a significant displacement of hydrogen from the surface by the substrate. An increase in pressure to 2 – 5 MPa alters the mechanism of the reaction, its rate at 20 °C becomes proportional to the concentration of 3-thiolene 1,1-dioxide (at $c = 0.07 – 0.7$ M), but is independent of hydrogen pressure.

Platinum. The hydrogenation of 3-thiolene 1,1-dioxide on supported platinum catalysts is slow.[44,45] In ethanol on the 4.8 mass % Pt/C catalyst, the yield of thiolane 1,1-dioxide was 81% with $W = 0.017$ mol h^{-1} g^{-1} (20 °C, $P = 0.1$ MPa, $c = 0.35$ M, $g_{ct} = 4.8$ g litre^{-1}, $t = 3.5$ h).[44] The industrial aluminoplatinum catalyst AP-56 also exhibited a low activity in isopropyl alcohol. The rate of reaction on this catalyst was 0.08 mol h^{-1} g^{-1} (20 °C, $P = 0.1$ MPa, $c = 0.4$ M, $g_{ct} = 20$ g litre^{-1}).[46] However, according to other data, catalysts containing 0.6 and 2 mass % of Pt on γ-Al_2O_3 have a much higher activity in isopropyl alcohol to which 10 mass % of thiolane 1,1-dioxide has been added. On these catalysts, $W = 1.1 – 1.2$ mol h^{-1} g^{-1} {20 °C, $P = 5$ MPa, $c = 0.4$ M, $[SO_2] < 0.03 \times 10^{-3}$ M}.[42] This discrepancy can apparently be accounted for by the fact that Mashkina *et al.*[42] hydrogenated a substrate from which sulfur dioxide had been thoroughly removed and carried out the reaction in the absence of diffusional complications, whereas these conditions were not maintained in the studies of Virobyants and coworkers.[44,45] In the hydrogenation of 3-thiolene 1,1-dioxide on platinum black under thoroughly controlled conditions, the 100% yield of thiolene 1,1-dioxide was attained after 1.5 min with $W = 1.5$ mol h^{-1} g^{-1} (20 °C, $P = 5$ MPa, $c = 0.37$ M, $g_{ct} = 10.7$ g litre^{-1}).[42] In the presence of platinum obtained by the reduction of its dioxide, the rate of hydrogenation per unit mass of the catalyst increases under the conditions indicated by a factor of 32, which can be explained by the increase in the specific surface of the metal. The activities of massive

platinum and platinum deposited on γ-Al_2O_3, calculated per unit surface, are the same (Table 2).

The rate of hydrogenation on platinum black at 20 °C in isopropyl alcohol to which 10 mass % of thiolane 1,1-dioxide has been added is proportional to the concentration of 3-thiolene 1,1-dioxide (P = 5 MPa, c = 0.05–0.6 M) and the hydrogen pressure (c = 0.4 M, P = 0.1–2 MPa).[42] At P > 2 MPa, the rate of reaction ceases to depend on the pressure. At atmospheric pressure on platinum black in ethanol, the reaction was found to be of first order with respect to 3-thiolene 1,1-dioxide (30–45 °C, c = 0.077 M). The increase in the rate of hydrogenation with increase in temperature is characterised by an activation energy of 22 kJ mol^{-1}.

The ratio of the concentrations of the reactants on the surface of the platinum catalyst was estimated in the course of the process by measuring the catalyst potential.[47] The reversible hydrogen potential of platinum, which is 600–660 mV, shifted by only 50 mV during the hydrogenation reaction. This permitted the conclusion that most of the catalyst surface is occupied by hydrogen and that the rate of reaction is limited by the activation of 3-thiolene 1,1-dioxide. In 0.1 N alcoholic solution of hydrochloric acid, the rate of hydrogenation is approximately twice as high as in a neutral medium and the reaction order with respect to thiophene 1,1-dioxide approaches zero.

Rhodium. Metallic rhodium exhibits a very high activity in the hydrogenation of 3-thiolene 1,1-dioxide.[42,48–50] In isopropyl alcohol to which 10 mass % of thiolane 1,1-dioxide has been added, exhaustive hydrogenation is attained on rhodium black after 0.5 min with W = 54 mol h^{-1} g^{-1} (at 20 °C P = 5 MPa, c = 0.37 M, g_{ct} = 8.6 g litre^{-1}).[48] When rhodium is deposited on a carrier, its activity becomes even higher. This can be explained by the increase in the degree of dispersion of the metal, which has been confirmed by data on the chemisorption of oxygen.[51] The degree of dispersion of supported rhodium is inversely proportional to its content, the greatest decrease in the degree of dispersion being observed on silicon dioxide (Table 3). The activity of the catalyst reduced by hydrogen at an elevated temperature can be increased by a factor of approximately four by treating it with air at 50–200 °C.[48,50] This effect has been explained by the removal of hydrogen strongly bound to the surface, which reacts with difficulty.[48] On treating the rhodium catalyst with air, rhodium oxide is not formed.

With increase in the degree of dispersion of the supported rhodium, the per activity of the catalyst per unit mass of the latter increases, whilst the activity per unit surface of the metal remains approximately constant and close to that of rhodium black (Table 3).

Kinetic studies have shown[42,48] that in the presence of rhodium black the increase in the rate of reaction with increase in temperature in the range 15–28 °C at P = 5 MPa and c = 0.4 M corresponds to an apparent activation energy of 34 ± 2 kJ mol^{-1}. When the content of 3-thiolene 1,1-dioxide is between 0.07×10^{-3} and 0.8×10^{-3} M, the rate of reaction (20 °C, P = 5 MPa) on rhodium black and on 5% Rh/Al_2O_3 is proportional to the concentration of the substrate. In the range of pressures P from 0.4 to 2 MPa (at 20 °C and c = 0.4 M), the rate of hydrogenation is proportional to the hydrogen pressure, whilst at a higher pressure (P = 2–7 MPa) it remains unchanged.

Nickel. The hydrogenation of 3-thiolene 1,1-dioxide in the presence of nickel catalysts has been investigated in fair detail. The patents published in the 1940s–1950s present numerous examples of hydrogenation on Raney nickel and nickel deposited on silicon dioxide.[52–56]

In the absence of a solvent, the yield of thiolane 1,1-dioxide on Raney nickel was ~30% and the hydrogenation was accompanied by the marked decomposition of the substrate (65 °C, P = 0.01 MPa, t = 20 h).[54] In solutions in ethanol, water, and thiolane 1,1-dioxide at 20–30 °C and $P \leqslant 0.01$ MPa, the yield of the target product increased to 58%–100% with W = 0.006–0.29 mol h^{-1},[52,53,56] In the presence of an excess of the catalyst, the 100% yield of thiolane 1,1-dioxide was attained already after 5 min (20 °C, $P \geqslant 30$ MPa, c = 4.24 M, g_{ct} = 170 g litre^{-1}), but for g_{ct} = 5 g litre^{-1} it did not exceed 85% even after 7 h.[55] On the 72% Ni/SiO_2 catalyst in thiolane 1,1-dioxide, exhaustive hydrogenation of 3-thiolene 1,1-dioxide in a flow system was attained at 27–30 °C, P > 7 MPa, and with the solution supplied at a space velocity of 3 h^{-1}.[54]

Table 3. The influence of the content of metallic rhodium in the supported catalyst on its specific surface, activity, and stability in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, P = 5 MPa, c = 0.4 M).[42,48]

Carrier	Content of Rh in catalysts/μg m^{-2}	S_{sp} /m^2 g^{-1} Rh	Activity		Stability	
			see [a]	see [b]	see [c]	see [d]
γ-Al_2O_3	30	280	250	175	–	–
	47	238	566	233	500	208
	125	217	916	208	833	175
	170	162	833	175	1250	250
	312	166	1670	200	1670	200
	570	139	3207	225	1670	200
SiO_2	78	86	242	142	–	–
	116	72	350	167	416	192
	195	57	500	175	670	233
AlSi	16	65	50	154	–	–
	31	–	100	–	160	–
	63	55	175	160	183	180
	115	–	250	–	–	–
	167	40	342	167	250	125
Activated charcoal	22	60	100	165	–	–
	41	60	200	167	170	140
	65	50	250	168	–	–
	102	40	330	170	250	125
Without carrier	170000	6	1850	306	1330	225

[a] Expressed in mol h^{-1} g^{-1}. [b] Expressed in mol h^{-1} m^{-2} Rh. [c] Expressed in mmol g^{-1}. [d] Expressed in mmol m^{-2} Rh.

Subsequently the study of this reaction in the presence of metallic nickel catalysts was continued. Unfortunately the results of different investigations do not always agree, possibly owing to the different degrees of purification of 3-thiolene 1,1-dioxide and the lack of monitoring of diffusional limitations.

According to the results of Virobyants and coworkers,[44,45] on Raney nickel at atmospheric pressure the hydrogenation of 3-thiolene 1,1-dioxide in solution in ethanol is slow and terminates only after 1.5–9.5 h (20 °C, c = 0.19–0.64 M, g_{ct} = 0.7–5 g litre−1). An increase in pressure facilitates the hydrogenation and, for example, in methanol the rate of reaction reaches 0.23 mol h^{-1} g^{-1}. The hydrogenation is slowest in thiolane 1,1-dioxide and water; in benzene, ethanol, and methanol, the reaction rates increase by factors of 2.5, 4, and 8 respectively (20 °C, P = 6 MPa, c = 1.7 M, g_{ct} = 6 g litre^{-1}). This agrees with other data,[57] according to which the rate of hydrogenation on Raney nickel in isopropyl alcohol is higher by a factor of 7–10 than in thiolane 1,1-dioxide (20 °C, P = 4 MPa). In the pressure range from 3 to 9 MPa, the rate of hydrogenation is proportional to P and at P = 7–14 MPa it changes little (20 °C, c = 1.4 M).[45] The slowness of the hydrogenation reaction of 3-thiolene 1,1-dioxide on Raney nickel even at an elevated hydrogen pressure has been confirmed by the results of Sapozhnikova *et al.*[58] An 87%–100% yield of thiolane 1,1-dioxide in isopropyl alcohol, thiolane 1,1-dioxide, or its mixture with water is attained after 6.5–8 h (30–40 °C, P = 10 MPa, c = 1.4 M). On the other hand, according to the results of Mashkina *et al.*[42] in the kinetic region on Raney nickel (S_{sp} = 70 m^2 g^{-1}) thiolane 1,1-dioxide was formed with 100% yield after only 11 min and the rate of

reaction was 0.3 mol h^{-1} g^{-1} {20 °C, P = 5 MPa, c = 0.4 M, g_{ct} = 7.2 g $litre^{-1}$, $[SO_2] < 0.03 \times 10^{-3}$ M}.

The modification of Raney nickel by adding metals increases its activity.[59] The catalytic properties are determined by the ratio Ni : Al in the alloy and by the method used to introduce additives. If the modification of nickel is carried out in the leaching stage by adding 0.1 mass % – 1 mass % of copper, cobalt, chromium, or platinum, the activity of the catalyst increases by a factor of 1.1 – 1.6, whereas in the presence of 0.1 mass % – 2 mass % of added vanadium and molybdenum the increase is by a factor of 1.5 – 3.0. The addition of molybdenum, vanadium, zirconium, or niobium to nickel in the fusion stage leads to the preparation of a catalyst the activity of which is higher by a factor of 3 – 6 than that of the unpromoted Raney nickel (Table 4). The surface of the nickel, determined from the degree of adsorption of thiophene, does not change as a result of the promotion.

Table 4. The influence of the promotion of Raney nickel on its catalytic properties in the hydrogenation of 3-thiolene 1,1-dioxide {20 °C, P = 5 MPa, c = 0.25 – 0.38 M, g_{ct} = 2.7 – 6.3 g $litre^{-1}$, $[SO_2] < 0.07 \times 10^{-3}$ M}.[59]

Promoting agent	Compound introduced into alkaline solution	Content of introduced promoting agent in catalyst (mass %)	Activity of catalyst [a]	Stability of catalyst [b]
Promotion of $NiAl_3$ alloy in the leaching stage [c]				
None	–	–	17.5	250
Cu	$Cu(NO_3)_2$	0.1 – 1	19.4	250
Cr	$Cr(NO_3)_3$	1.0	27.7	290
Mo	$(NH_4)_2MoO_4$	0.1	6.7	275
Co	$Co(NO_3)_2$	0.1 – 1	22.3	217
V	NH_4VO_3	1.0	51.6	583
Pt	H_2PtCl_6	0.1 – 1	28.3	267
Promotion of the NiAl alloy in the leaching stage [c]				
None	–	–	11.7	50
V	V_2O_5	0.25	16.7	100
V	NH_4VO_3	0.6	34.2	125
Promotion in the fusion stage [d]				
None	–	–	4.5	33
Mo	–	1.0	13.3	200
Mo	–	7.5	21.7	183
Zr	–	1.0	18.3	130
Nb	–	1.0	28.7	233
V	–	4.7	13.3	83
V	–	14.8	16.7	117

[a] Expressed in mol h^{-1} g^{-1}. [b] Expressed in mmol g^{-1}. [c] Leaching conditions: 50 °C, [KOH] = 25 mass %. [d] Leaching conditions: 100 °C, [KOH] = 15 mass % – 25 mass %.

The Raney nickel catalyst obtained from a Ni – Al alloy doped with a series of metals exhibits an enhanced activity also in the hydrogenation reactions of other unsaturated compounds.[60] It has been postulated that doping with niobium and zirconium leads to an increase in the content of the intermetallic compound $NiAl_3$ in the alloy; molybdenum aluminides, which influence the degree of dispersion of nickel, are formed in the molybdenum-containing alloys.[61] Doping of vanadium-containing alloys alters the energy of the bond between hydrogen and the surface and the rate of production of hydrogen.[62]

Nickel on a carrier is also used as a catalyst of the hydrogenation of 3-thiolene 1,1-dioxide. In the presence of 50 mass % of nickel on chromium trioxide or silicon dioxide, the initial rate of reaction (1 min after its onset) in isopropyl alcohol at atmospheric pressure is 0.10 – 0.15 mol h^{-1} g^{-1}, but exhaustive hydrogenation is attained only after 1 h and the average rate of reaction over this period is only 0.017 mol h^{-1} g^{-1} (20 – 30 °C, c = 0.42 M, g_{ct} = 20 g $litre^{-1}$).[46, 63 – 66] The addition of platinum to the nickel – chromium catalyst does not alter its activity.[67, 68] An increase in pressure promotes an increase in the rate of hydrogenation of 3-thiolene 1,1-dioxide, which is 0.19 – 0.33 mol h^{-1} g^{-1} at P = 2 – 5 MPa (20 – 35 °C, c = 0.4 – 1 M).[64, 65]

The kinetics of the hydrogenation of 3-thiolene 1,1-dioxide on Raney nickel and on the nickel – chromium catalyst are approximately the same.[46, 47, 57, 63 – 65, 69 – 72] In the hydrogenation of pure 3-thiolene 1,1-dioxide {$[SO_2] < 0.03 \times 10^{-3}$ M}, the reaction takes place in the kinetic region, provided that the catalyst grain size does not exceed 0.1 mm. The reaction order depends on the substrate concentration and hydrogen pressure ranges.

At atmospheric pressure, the reaction is of zero order with respect to 3-thiolene 1,1-dioxide dissolved in isopropyl alcohol or thiolane 1,1-dioxide in the concentration ranges c = 0.5 – 5 M (35 °C, Ni/Cr_2O_3) and c = 0.1 – 0.8 M (20 °C, Raney nickel).[63, 70] On the other hand, when the reaction was carried out in another study [47] on Raney nickel in ethanol, it was found to be of first order with respect to 3-thiolene 1,1-dioxide ($c \leqslant 0.07$ M, 15 – 45 °C). At an elevated pressure, the reaction order with respect to 3-thiolene 1,1-dioxide changes from zero in the range c = 1.5 – 5.3 M (30 °C, P = 0.7 – 4 MPa) to first in the range c = 0.1 – 2.5 M (30 – 35 °C, P = 0.7 – 4 MPa). The reaction order with respect to hydrogen also changes from first in the pressure range 0.01 – 2.5 MPa (20 – 35 °C, c = 0.53 – 3 M) to zero at P = 0.7 – 4 MPa (30 – 35 °C, c = 0.53 – 3 M).[57, 63, 64, 70]

The dependence of the reaction order on Raney nickel on the reaction conditions has been explained by the change in the mechanism of the hydrogenation of 3-thiolene 1,1-dioxide.[57] At $P \leqslant 0.1$ MPa (zero order with respect to the substrate and first order with respect to hydrogen), 3-thiolene 1,1-dioxide is hydrogenated under conditions where its concentration in solution greatly exceeds the concentration of hydrogen owing to the low solubility of the latter. The ratio of the reactant concentrations on the catalyst surface during the reaction at P = 0.1 MPa may be inferred from the change in the catalyst potential. The reversible hydrogen potential of Raney nickel is 540 – 610 mV (30 °C). When 3-thiolene 1,1-dioxide is introduced into the solution, the potential shifts to the anodic region by a 300 – 400 mV,[47, 57, 65] which indicates the preferential adsorption of the substrate and the displacement of a large proportion of hydrogen from the surface by the latter. The 3-thiolene 1,1-dioxide substrate is rapidly adsorbed on nickel and the limiting degree of its adsorption from solutions is $\sim$ 0.2 g per gram of nickel. Under these conditions, the degree of surface coverage of nickel by 3-thiolene 1,1-dioxide is high and the rate of hydrogenation is therefore independent of the substrate concentration. The rate of the process is limited by the activation of hydrogen.[57] Sokol'skaya and Reshetnikov,[47] who investigated the hydrogenation of 3-thiolene 1,1-dioxide in ethanol on Raney nickel (15 – 45 °C, P = 0.1 MPa, c < 0.1 M), arrived at the same conclusion. At pressures above atmospheric, the concentration of hydrogen in solution and on the nickel surface increases and the reactant ratio on the surface changes, which affects the reaction mechanism.

In order to account for the observed kinetics in the absence of diffusional complications, one employs the kinetic schemes for liquid-phase hydrogenation reactions on inhomogeneous surfaces and the corresponding specific kinetic equations.[73] It has been suggested that there is equilibrium between the concentrations of the reactants on the surfaces and in the liquid phase. The lack of dependence of the rate of hydrogenation of 3-thiolene 1,1-dioxide on the of the weight of the catalyst sample permitted the conclusion that the rate of the process is not limited by the dissolution of hydrogen and that one may use instead of the hydrogen concentration in solution the hydrogen pressure, which is proportional to it.

The first order of the reaction with respect to the substrate at a constant hydrogen pressure, the high rate of adsorption of

3-thiolene 1,1-dioxide,and the occurrence of the reaction at high surface coverages by the substance hydrogenated [57] provide grounds for the hypothesis that at $c \leqslant 1.6$ M the reaction takes place in accordance with the Scheme 4.

Scheme 4

$$H_2\,(sol) \rightleftharpoons 2H\,(ads),$$

$$2H\,(ads) + \underset{SO_2}{\square}\,(sol) \rightleftharpoons \underset{SO_2}{\square}\,(sol).$$

If the rate of reaction is limited by the interaction of the dissolved 3-thiolene 1,1-dioxide with the adsorbed hydrogen and the reaction proceeds at high surface coverages by hydrogen, its rate is described by the equation

$$W = kc_1 .$$

Here c_1 is the concentration of 3-thiolene 1,1-dioxide and

$$k = \frac{(\vec{k}_2)_0}{m'},$$

where $(\vec{k}_2)_0$ is the rate constant for the second stage in the forward direction and m' is a constant characterising the degree of inhomogeneity of the catalyst surface.

The overall zero order of the reaction with respect to both reactants, observed under the conditions of hydrogenation of Raney nickel at a high 3-thiolene 1,1-dioxide concentration in solution and an elevated hydrogen pressure, has been explained [47] by the occurrence of the reaction *via* a stage involving the formation of a complex incorporating hydrogen, 3-thiolene 1,1-dioxide, and nickel (Scheme 5).

Scheme 5

1. $\underset{SO_2}{\square}\,(sol) + H_2\,(sol) + [Ni] \longrightarrow \underset{SO_2}{\square}\cdot H_2\cdot[Ni]$

2. $\underset{SO_2}{\square}\cdot H_2\cdot[Ni] = \underset{SO_2}{\square}\,(sol) + [Ni]\,.$

If the process is limited by the consumption of the complex (stage 2) and proceeds at a high surface coverage by both reactants, its rate is described by the equation

$$W = k\,,$$

where $k = \dfrac{(\vec{k}_2)_0}{m'}$.

In a flow system on large 50% Ni/Cr_2O_3 catalyst grains, the rate of hydrogenation of 3-thiolene 1,1-dioxide is lower than in a static system on fine grains.[64, 69, 71, 72, 75] The rate of hydrogenation increases with decrease in the catalyst grain size and with increase in the linear rate of supply of the starting material. The activation energy is only 8.4 kJ mol^{-1}. These results indicate that the reaction proceeds in the external diffusion region. At $c = 1.06-2.65$ M and $P < 0.6$ MPa, the rate of hydrogenation is proportional to the hydrogen pressure and is independent of the concentration of 3-thiolene 1,1-dioxide. Under these conditions, the process is limited by the rate of supply of hydrogen to the outer surface of the catalyst (external diffusion region with respect to hydrogen). At pressures exceeding 0.6 MPa, the rate of supply of hydrogen to the surface increases and the rate of reaction ceases to depend on the hydrogen pressure (zero order with respect to hydrogen) but becomes proportional to the concentration of 3-thiolene 1,1-dioxide. The slowest stage determining the rate of hydrogenation becomes the rate of arrival of the substrate on the outer surface of the catalyst, *i.e.* the process passes to the external diffusion region with respect to 3-thiolene 1,1-dioxide.

In the kinetic region, the rate of reaction in a flow reactor is expressed by the equation

$$W = kHXP\,,$$

where k is the reaction rate constant, H the solubility coefficient of hydrogen, the X concentration of hydrogen, and P the pressure.

On the other hand, if the rate of mass transfer is less than the rate of reaction and the process proceeds either at low hydrogen concentrations or low 3-thiolene 1,1-dioxide concentrations, then the equations for the rate of reaction assume the following forms respectively:

$$W = aHk_1P \quad \text{and} \quad W = k_2X\,,$$

where a is the stoichiometric coefficient and k_1 and k_2 are the mass transfer coefficients of hydrogen and 3-thiolene 1,1-dioxide respectively in the direction of the diffusion flux. These equations describe satisfactorily the experimental data on the hydrogenation of 3-thiolene 1,1-dioxide to thiolane 1,1-dioxide in a flow reactor.

Since under the conditions where the reaction takes place in the external diffusion region with respect to hydrogen the flow reactor becomes similar to the packed column employed for the adsorption of gases, the equations for mass transfer in a film adsorber may be employed for the calculations if it is assumed that the catalyst assumes the role of the packing and the column operates in the film regime.[69, 71] The principal technological parameters of the process have been selected and a scheme for the synthesis of thiolane 1,1-dioxide has been recommended on the basis of a detailed study of the kinetics of the hydrogenation of 3-thiolene 1,1-dioxide on the nickel-chromium catalyst.[64, 69, 75]

Palladium. In the early studies (see the present author's previous review [1]), it was already noted that, in the presence of metallic palladium catalysts, the multiple bond of 3-thiolene 1,1-dioxide is fully saturated and thiolane 1,1-dioxide is formed in 100% yield. At atmospheric pressure in aqueous solution on colloidal palladium, the reaction is slow with the rate $W = 0.004$ mol h^{-1} g^{-1} (20 °C, $c = 0.2$ M, $g_{ct} = 250$ g $litre^{-1}$).[4] When palladium is deposited on charcoal, the rate of reaction in ethanol increases to 0.017–0.05 mol h^{-1} g^{-1} (20 °C, $c = 0.35-1.0$ M).[44, 76] In the presence of 5% $Pd/BaSO_4$ in ethanol, exhaustive hydrogenation takes place over a period of 3–4 min (30 °C, $P = 0.1$ MPa, $c = 0.077$ M, $g_{ct} = 1.72$ g $litre^{-1}$) at the rate $W = 0.92$ mol $h^{-1}g^{-1}$.[47]

At an elevated pressure, the rate of hydrogenation of purified 3-thiolene to which 1,1-dioxide in the kinetic region in isopropyl alcohol 10 mass % of thiolane 1,1-dioxide has been added increases appreciably. Thus on palladium black the 100% yield of thiolane 1,1-dioxide is attained after less than 1 min and $W = 13.7$ mol h^{-1} g^{-1} {20 °C, $P = 5$ MPa, $c = 0.37$ M $[SO_2] = 0.028 \times 10^{-3}$ M}.[42] Under these conditions, the reaction rates are 4.2, 4.0, 3.4, and 1.3 mol h^{-1} g^{-1} on catalysts containing 2 mass % of Pd on γ-Al_2O_3, AlSi, SiO_2, and activated charcoal respectively.[77]

The rate of hydrogenation of 3-thiolene 1,1-dioxide is influenced by the nature of the solvent. On the 5% Pd/Al_2O_3 (20 °C, $P = 5$ MPa, $c = 0.4$ M) in isopropyl alcohol, the reaction was very rapid, in 1-butanol the rate of hydrogenation fell by a factor of 1.2, and in *tert*-butyl alcohol and thiolane 1,1-dioxide it fell by a factor of 10.[78] In a mixture of isopropyl alcohol and 5 mass %–20 mass % of thiolane 1,1-dioxide, the rate of reaction was the same as in pure isopropyl alcohol. The addition of 2 mass %–10 mass % of water to isopropyl alcohol reduces the rate of hydrogenation by a factor of 1.2–2.5. In isopropyl alcohol, the rate of reaction is a maximum in a neutral medium, the rate diminishing approximately by a factor of 2 when potassium hydroxide or hydrochloric acid is added to the solution at a concentration of 2.5×10^{-3} M.[78]

The kinetics of the hydrogenation of 3-thiolene 1,1-dioxide in pure isopropyl alcohol or isopropyl alcohol to which 10 mass % of thiolane 1,1-dioxide had been added were investigated on palladium-containing catalysts of different compositions.[42, 78, 79]

On palladium black and on the 2.5% Pd/Al_2O_3 catalyst, the reaction takes place in the kinetic region where the grain size is 0.06–0.1 mm (20 °C, $P = 5$ MPa, $c = 0.4$ M). On catalysts of

different composition in the range of pressures P from 0.1 to 1.0 MPa, the rate of hydrogenation at 20 °C and $c = 1.4$ M is proportional to the hydrogen pressure, but at pressures in the range 1–6 MPa it remains constant. At $P = 5$ MPa, the rate of hydrogenation is proportional to the concentration of 3-thiolene 1,1-dioxide (at $c = 0.1-1$ M), but at $P = 0.1$ MPa it remains unchanged in the range of concentrations c from 0.04 to 0.21 M.[42, 78, 79] However, it has been found[47] that the rate of hydrogenation of 3-thiolene 1.1-dioxide on the 5% $Pd/BaSO_4$ catalyst in ethanol is proportional to the substrate concentration (at $c < 0.077$ M); the activation energy for the reaction was 19 kJ mol^{-1} (15–45 °C, $P = 0.1$ MPa).

The mechanism of the hydrogenation of 3-thiolene 1,1-dioxide on palladium-containing catalysts is apparently the same as on nickel catalysts.[47, 48] The necessary stages of the formation of thiolane 1,1-dioxide are the adsorption of the reactants and their activation on the catalyst surface.

The adsorption of 3-thiolene 1,1-dioxide on palladium at 20 °C and $P = 0.1$ MPa is very rapid and its rate cannot therefore be determined. The ratio of the surface concentrations of the reactants during the reaction was estimated by measuring the catalyst potential at atmospheric pressure in alcoholic solutions.[47, 67]

The reversible hydrogen potential of the palladium catalyst is 630–640 mV. After the introduction of 3-thiolene 1,1-dioxide into a neutral solution, the potential shifted to the anodic region by 100–120 mV (5% $Pd/BaSO_4$, 30 °C, $c = 0.077$ M, solution in ethanol)[47] or by 130 mV (2% Pd/C, 20 °C, $c = 0.25$ M, solution in isopropyl alcohol).[67] According to the existing ideas,[47] such a potential shift indicates a relatively weak bond between hydrogen and the catalyst and the displacement of hydrogen from the surface by the adsorbed 3-thiolene 1,1-dioxide and also a high surface coverage by the dioxide.

In principle, it is possible that at $P > 2$ MPa the reaction proceeds *via* an impact mechanism, *i.e. via* the interaction of molecular hydrogen with the adsorbed 3-thiolene 1,1-dioxide. However, in this case the rate of hydrogenation should have depended on the hydrogen pressure. Since this conflicts with experimental results, it was concluded[47] that the hydrogen adsorbed on the palladium surface participates in the reaction.

Hydrogen, which can be adsorbed on palladium at a high rate,[39] can participate in the hydrogenation. Thus, on hydrogen-saturated palladium black (20 °C, $P = 0.1$ MPa, $t = 30$ min) in nitrogen, 3-thiolene 1,1-dioxide is hydrogenated at a rate of 14 ml H_2 min^{-1} g^{-1}. However, this is an order of magnitude less than the rate of hydrogenation in a H_2 atmosphere, *i.e.* the hydrogen dissolved in palladium hydrogenates only part of the substrate and a continuous resupply of the surface by hydrogen is required. The strength of the bond between hydrogen and the catalyst should then lie within definite limits.[39, 78] This has been confirmed by the results of experiments on hydrogenation on palladium-containing catalysts in which the bond between hydrogen and palladium was changed by means of modifying additives.[80] Thus, on a hydrogen-saturated 1.5% Pd + 0.5% Pt/C specimen, the anodic potential shift on hydrogenation of 3-thiolene 1,1-dioxide is 90 mV, *i.e.* smaller by 40 mV than on an unpromoted 2% Pd/C specimen.[67] This indicates a strengthening of the bond between hydrogen and the surface. The rate of hydrogenation of 3-thiolene 1,1-dioxide in isopropyl alcohol on the promoted catalyst decreases from 0.032 to 0.018 mol h^{-1}g^{-1} (20 °C, $P = 0.1$ MPa, $c = 0.254$ M). The introduction of alkali into the hydrogenated solution leads to the formation of an unduly strong bond between hydrogen and the palladium surface[39] and the activity of the catalyst diminishes. Thus, on the 4% Pd/Al_2O_3 catalyst the rate of hydrogenation of 3-thiolene 1,1-dioxide in a neutral solution is higher by a factor of 3 than after the addition of sodium hydroxide at a concentration of 2.25×10^{-3} M (20 °C, $P = 5$ MPa, $c = 0.4$ M).[22]

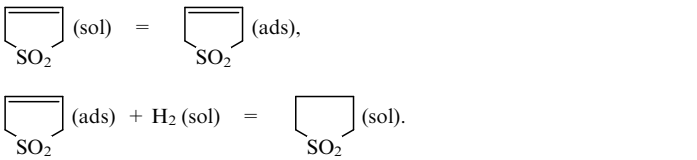
Under the conditions of the reduction of the catalyst at an elevated temperature (300 °C), a strong hydrogen–palladium bond is formed and such hydrogen is insufficiently reactive and is desorbed with difficulty.[81] Its removal from the surface *in vacuo* (10^{-3} mm Hg at 300 °C, $t = 20$ h) or on treatment with air (50–250 °C, $t = 2$ h) increases the activity of the catalyst in the hydrogenation of 3-thiolene 1,1-dioxide by a factor of 2.[82] On comparing the specific surfaces of palladium found from the chemisorption of oxygen and by the method involving the poisoning of the catalyst during hydrogenation, one may conclude that the increase in activity is due to the increase in the number of active sites on the surface after the removal of hydrogen by oxidative treatment.

On palladium black and supported catalysts (2 mass % – 10 - mass % Pd/γ-Al_2O_3) the reaction orders with respect to hydrogen and 3-thiolene 1,1-dioxide in isopropyl alcohol with added 10% of thiolane 1,1-dioxide depend on the hydrogenation conditions (see above).

The activity of palladium decreases after the introduction into the hydrogenated solution of very small amounts of sulfur dioxide and hydrogen sulfide. The exponential decrease in the activity of the catalyst with increase in the concentration of the poison in solution observed under these conditions is associated with the energy inhomogeneity effect in the real adsorbed layer.

The kinetics observed on palladium catalysts have been examined in a generalised form.[78] At low pressures ($P = 0.1-1$ MPa), the concentration of 3-thiolene 1,1-dioxide in solution appreciably exceeds the concentration of hydrogen because of the low solubility of the latter. Under the reaction conditions, the substrate displaces hydrogen from the surface and the latter proves to be saturated by 3-thiolene 1,1-dioxide. It is most likely that the reaction proceeds in accordance with the Scheme 6.

Scheme 6



The zero order of the reaction with respect to 3-thiolene 1,1-dioxide and the first order with respect to hydrogen can be accounted for by the limitation of the process by the stage involving the interaction of the adsorbed substrate with hydrogen. The kinetic equation assumes the following form in this instance:

$$W = k,$$

where $k = \dfrac{(\overrightarrow{k_2})_0 c_2}{m'}$.

At a hydrogen pressure in excess of 2 MPa, the process kinetics change owing to the alteration of the reaction mechanism. It has been suggested[78] that an increase in pressure promotes an increase in the concentration of hydrogen in solution and facilitates its access to the catalyst surface. This induces an increase in the degree of surface coverage by hydrogen, which becomes comparable to the degree of surface coverage by the substrate. In this case, the process is described by the kinetic equation which follows from Scheme 4.

The activity of palladium-containing catalysts in the hydrogenation reaction of 3-thiolene 1,1-dioxide depends significantly on the area of the accessible palladium surface. Massive palladium, obtained by the reduction of an aqueous solution of palladium chloride by formalin in an alkaline medium, is characterised by $S_{sp} = 5$ m^2 g^{-1}, while the specimen prepared by oxidising palladium chloride with sodium nitrate and subsequent reduction with hydrogen is characterised by $S_{sp} = 22$ m^2 g^{-1}. The activities of these catalysts per gram of palladium (20 °C, $P = 5$ MPa, $c = 0.4$ M) are significantly different (466 and 1850 mol h^{-1} g^{-1} respectively), but their activities per unit surface are similar (93 and 84 mol h^{-1} m^{-2} Pd respectively).[42]

It has been established that the degree of dispersion of palladium on carriers exerts a strong influence on the activity of hydrogenation catalysts.[77, 79, 83] The degree of dispersion of palladium was measured by several independent methods: by X-ray phase analysis (XPA), by electron microscopy (EM), from the chemisorption of oxygen, carbon monoxide, and sulfur dioxide, and by the method involving the poisoning of the catalyst by a sulfur poison in the course of hydrogenation. All the methods yielded similar degrees of dispersion of palladium. It follows from the data obtained that most of the palladium is in the crystalline state. The degree of dispersion of palladium depends on its content in the catalyst, the nature of the carrier, its specific surface, the method of preparation of the specimen, and the presence of certain additives.

Palladium deposited on alumina, aluminosilicate, and activated charcoal has a high degree of dispersion, whilst palladium deposited on a zeolite, corundum, and carborundum has a low degree of dispersion (Tables 5 and 6).[77, 79, 83, 84]

Table 6 shows that the degree of dispersion of palladium increases linearly with decrease in its surface concentration. The smallest change in the degree dispersion as a function of the metal concentration on the surface is observed when palladium is deposited on activated charcoal and the greatest change is observed when it is deposited on silicon dioxide. This difference can be explained by the different strengths of the Pd – carrier bond and the associated difference between the surface mobilities of palladium. However,on the whole the overall surface area of the metal increases up to a certain limiting content of the metal on the carrier and the rate of hydrogenation of 3-thiolene 1,1-dioxide calculated per unit mass of the catalyst therefore increases.

For a constant content of palladium, the degree of its dispersion may be regulated not only by varying the nature of the carrier but also by varying the composition of the impregnating solution and by subjecting the specimen to an additional chemical treatment before reduction. We shall consider this in relation to the Pd/Al_2O_3 catalyst prepared by impregnating the carrier with an aqueous solution of a palladium compound with subsequent reduction by hydrogen at 300 °C for 30 h.[84–88] The degree of dispersion of palladium in specimens obtained by employing a palladium chloride solution in hydrochloric acid proved to be various (Table 6). In the presence of an excess of hydrochloric acid ($HCl : PdCl_2 = 2 : 1$), the Pd^{2+} complex contains only chloride ligands, is weakly bound to the γ-Al_2O_3 surface, and is relatively mobile. Its heat treatment therefore results in the formation of comparatively large palladium agglomerates (specimen No. 1 in Table 6). For the ratio $HCl : PdCl_2 = 1 : 1$ (specimen No. 2), the composition of the palladium ion complex includes also OH groups, which promotes stronger binding of palladium to the γ-Al_2O_3 surface and hence a decrease in the degree of crystallisation of the metal. However, unduly strong binding of the Pd^{2+} ion to the carrier, as happens for example when the $Pd(NH_3)_4Cl_2$ complex is employed (specimen No. 3), makes it necessary to increase the reduction temperature to 400 °C and this tends to intensify crystallisation and promotes a sharp decrease in the degree of dispersion of palladium. Aluminium oxide impregnated with a hydrochloric acid solution of $PdCl_2$ and subjected to an additional treatment with potassium

Table 5. Dependence of the specific surface of palladium, its activity, and its stability on the composition of the catalyst (20 °C, $P = 5$ MPa, $c = 0.4$ M).[77, 83]

Carrier	S_{BET} /$m^2\ g^{-1}$	Surface concentration of Pd /$\mu g\ m^{-2}$	S_{sp} /$m^2\ g^{-1}$ Pd	Activity		Stability	
				mol $h^{-1}\ g^{-1}$	mol $g^{-1}\ m^{-2}$ Pd	mmol g^{-1}	mmol m^{-2} Pd
γ-Al_2O_3	200	25	280	83	62	–	–
	200	50	220	185	87	250	113
	200	100	195	292	75	417	107
	200	150	160	416	88	500	104
	200	250	140	580	83	670	95
	200	400	125	830	85	–	–
	200	500	130	1000	67	1330	103
	200	750	100	1460	96	–	–
	200	1000	80	1450	92	–	–
	242	83	210	330	79	417	100
	119	170	110	217	98	242	110
	81	247	80	133	83	158	99
SiO_2	300	17	100	25	50	–	–
	300	33	80	45	58	67	83
	300	67	60	67	56	–	–
	300	100	45	85	60	125	88
	300	167	30	127	83	–	–
	300	267	30	167	70	–	–
AlSi	360	14	314	100	63	–	–
	360	27	280	133	50	250	92
	360	56	200	200	50	–	–
	360	83	130	250	64	330	83
	360	140	100	333	42	–	–
Activated charcoal	510	20	195	108	54	250	67
	510	40	165	210	63	–	–
	510	60	210	290	45	500	83
	510	100	170	351	42	–	–
NaX	–	30	–	50	–	–	–
CaX	–	30	–	56	–	–	–
NaY	–	28	–	43	–	–	–

Table 6. The influence of the method of preparation of the 5% Pd/Al_2O_3 catalyst on the degree of dispersion of palladium, its activity, and its stability in the hydrogenation of 3-thiolene 1,1-dioxide.[84,85]

No. of Specimen	S_{sp} /m^2 g^{-1} Pd	Pd particle size /nm			Activity		Stability	
		chemisorption of O_2	XPA	EM	mol h^{-1} g^{-1}	mol h^{-1} m^{-2} Pd	mmol g^{-1}	mmol m^{-2} Pd
1	100	6.0	10.0	11	500	100	500	100
2	140	3.5	8.0	10	580	83	660	96
3	20	20.0	24.0	25	60	58	–	–
4	180	2.5	(see [a])	–	750	88	1170	117
5	180	2.3	(see [a])	–	833	87	–	–
6	210	2.0	(see [a])	–	100	100	1160	118
7	180	2.3	(see [a])	–	830	92	100	108

[a] X-Ray-amorphous specimen.

hydroxide, sodium carbonate, or hydrogen sulfide before reduction with hydrogen (specimens Nos 4–6) or the same specimen impregnated with palladium nitrate (No. 7) contain a water-insoluble palladium oxide or sulfide, which reduces the mobility of the metal on the surface during reduction and promotes an increase in its degree of dispersion.

With increase in the specific surface of palladium, its activity in the hydrogenation of 3-thiolene 1,1-dioxide per unit mass of the specimen also increases, *i.e.* from the standpoint of increasing the productivity of the catalyst it is convenient to employ specimens with a higher palladium content on the carrier. However, the activity per m^2 of the palladium surface when the size of the crystallites is up to 20 Å remains approximately constant (within the limits of 20 rel. %) and hardly differs from the specific activity of palladium black (Tables 5 and 6). Thus in this case too Boreskov's rule holds.[74] According to this rule, the specific catalytic activities of catalysts having the same composition are approximately constant.

In many instances, the degree of dispersion of palladium increases when other elements are added to it.[67,89,93] The addition of 3 mass % of boron to palladium black or the 5% Pd/Al_2O_3 catalyst increases the specific surface of palladium and the activity of the catalyst per unit mass of the latter increases by a factor of 1.5–2.[89,93] In order to increase the activity of palladium (both massive and deposited on γ-Al_2O_3), it has been suggested that other Group VIII metals be added to the catalyst.[67,90,93] The activity depends on the concentration of the additive introduced and passes through a maximum at a definite content of the latter (Table 7). The passage of the catalytic activities of mixed palladium-containing catalysts through a maximum as a function of composition has been observed also in the hydrogenation of other unsaturated compounds. This phenomenon has been unambiguously explained.[39] It has been postulated that the additives alter the amount and form of the sorbed hydrogen and also the energy of its bond with the surface. However, it is difficult to test this experimentally. It may be that the alloy should have a definite electronic structure and that an activity maximum is attained when the number of vacancies in the *d* layer per metal atom is unity.[39] However, contrary to experimental data, a catalytic activity maximum should not be observed in this case on Pd–Pt alloys, since both metals have the same number of vacancies (0.6). The additives can influence the electronic configuration of palladium or can alter the degree of its dispersion.[91,92]

It is difficult to determine the surface areas of two different supported metals separately. Therefore, in order to justify the important role of the degree of dispersion of palladium, indirect evidence, obtained in a study of mixed oxides without a carrier which are solid solutions according to XPA data, was resorted to.[67,93] It was found that the activity of palladium oxide (S_{sp} = 25 m^2 g^{-1}) in the hydrogenation of 3-thiolene 1,1-dioxide is very high and amounts to 1700 mol h^{-1} g^{-1}, so that complete reduction is attained after 1 min (20 °C, P = 5 MPa, c = 0.38 M, g_{ct} = 0.54 g $litre^{-1}$). The palladium oxide is then fully reduced to the metal. Ruthenium and iridium oxides (S_{sp} = 114 and 162 m^2 g^{-1} respectively) are appreciably less active under the conditions indicated (54 and 2.5 mol h^{-1} g^{-1} respectively), while rhodium oxide (S_{sp} = 160 m^2 g^{-1}) is completely inactive. Ruthenium and iridium oxides are reduced much more slowly in alcohol

Table 7. The influence of the modification of palladium catalysts on their activity and stability in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, P = 5 MPa, c = 0.38 M).[67,89,93]

Modifying agent	Content in catalyst (mass %)		S_{sp} /m^2 g^{-1}	Activity [a]	Stability /mmol g^{-1}
	Pd	modifying agent			
Pd/γ-Al_2O_3					
None	5.0	0	140 [b]	583	667
B	4.85	0.15	200 [b]	830	1000
Mn	4.75	0.25	–	900	1250
	4.5	0.5	–	900	1125
Ru	4.5	0.5	–	1024	1000
Rh	4.5	0.5	–	1170	1165
Ir	4.75	0.25	–	1083	830
Pt	4.25	0.75	–	1025	917
Pd without carrier					
None	100	0	5	575	1330
Ru	90	10	17	1450	1830
	75	25	58	2810	2500
	50	50	78	1930	–
	20	80	130	762	–
	0	100	114	54	250
Pt	95	5	18	2540	–
	85	15	24	3920	1670
	50	50	37	4600	–
	25	75	81	4230	1665
	0	100	88	2300	–
Rh	90	10	45	3024	2917
	75	25	74	3215	5000
	50	50	104	5048	6670
	30	70	103	1400	1670
	20	80	96	174	–
	0	100	162	0	–
Ir	95	5	37	3465	1667
	90	10	43	3265	1670
	75	25	51	408	–
	0	100	162	8	–

[a] Expressed in mol h^{-1} g^{-1}. [b] The specific surface of palladium. In the remaining cases, the specific surface of the catalyst determined by the BET method is given.

at 20 °C than palladium oxide. The complete reduction of Rh_2O_3 by hydrogen to metallic rhodium does not occur until 300 °C over a period of 2 h. Under the conditions of brief (0.5–1 min) saturation of the catalyst with hydrogen before the experiment and when 3-thiolene 1,1-dioxide is hydrogenated during the same period, only palladium oxide is reduced but not the oxides of other metals. The overall surface area of palladium and other platinum group metals in the mixed catalyst is greater than the surface area of unpromoted palladium. One may therefore assume that the increase in the activity of the catalyst in the presence of additives is associated with the increase in the degree of dispersion of palladium. A similar conclusion was reached also in the study of other palladium-containing bimetallic systems. When ruthenium is introduced into PdC or when lanthanum is introduced into Pd/SiO_2, the degree of dispersion of palladium increases.

V. The resistance of metallic catalysts to sulfur

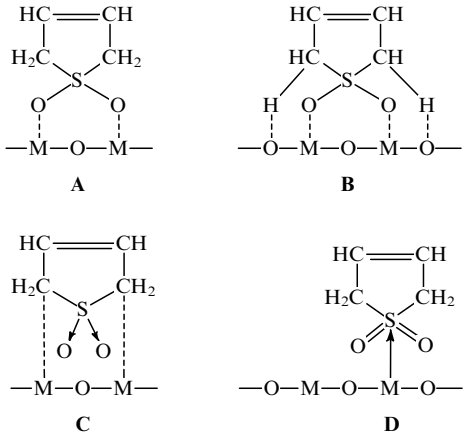
For metallic catalysts used in the low-temperature hydrogenation of various unsaturated substances, sulfur compounds are frequently catalytic poisons. The metal is deactivated as a result of the competitive chemisorption of the poison on the active centres (see the relevant reviews [94–97]).

Sulfur compounds are strongly chemisorbed on the metal, forming a donor-acceptor bond with the latter.[94] Compounds of bivalent and tetravalent sulfur, having lone electron pairs, can participate in this process. However, sulfur-containing molecules lose their toxicity when all the valence orbitals of sulfur are saturated as a result of the formation of strong bonds with other elements, as happens, for example, in hexavalent sulfur compounds. The decrease in activity may be caused also by the change in the composition of the catalytically active component. Thus the interaction of hydrogen sulfide or certain organic sulfur compounds with the metal may entail the formation of the metal sulfide, which only weakly activates hydrogen and therefore exhibits a low activity in low-temperature hydrogenation processes.[15]

The chemical properties of sulfones have been considered in a number of studies.[6, 40, 98] The sulfur atom of the sulfone has no lone pairs and therefore has no electron-donating capacity. The bond between sulfur and oxygen is mainly semipolar (O ← S) but it also has partial double bond character (the $p_\pi - d_\pi$ O=S bond). It is formed as a result of the interaction of the lone pair of oxygen with the unoccupied *d* orbital of the sulfur atom. The presence of a large positive charge on the sulfur atom increases the capacity of sulfones for $p-d$ conjugation and this tends to increase the acidity of the α-hydrogen atom of the sulfone. The oxygen atom in the sulfone has excess negative charge and this permits the formation of adducts *via* the oxygen atom. Thus metal compounds in solution form a donor–acceptor bond with charge transfer from the oxygen atom of sulfonyl group to the metal atom.[14, 98].

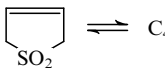
Knowing the properties of sulfones, one may put forward a hypothesis concerning the probable surface forms of 3-thiolene 1,1-dioxide formed when it comes into contact with the metal and the carrier. Apart from the π-olefin complex, the formation of which activates the multiple bond and leads to its reduction with formation of thiolane 1,1-dioxide (see Scheme 3), other surface structures can also arise (Scheme 7). The formation of bonds between the metal and the oxygen atoms of the sulfonyl group (**A**) is most probable. There is also a possibility of the coordination of the α-hydrogen atoms of the sulfone to the oxygen atoms of the carrier (**B**) and of the α-carbon atoms to the metal atoms (**C**) as well as the formation of a complex as a result of the interaction of the electrons of the metal atom with the d orbital of sulfur

Scheme 7



(a $d_\pi - d_\pi$ bond) (**D**). The formation of a complex on the catalyst surface may entail the weakening and dissociation of the C–S bonds in the 3-thiolene 1,1-dioxide molecule.[14]

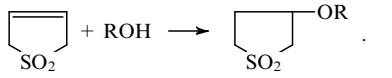
On dissociation of both C–S bonds in 3-thiolene 1,1-dioxide, buta-1,3-diene and sulfur dioxides are formed.



$\rightleftharpoons C_4H_6 + SO_2.$

This reaction occurs even at room temperature and is accelerated as the temperature is raised. Above 100 °C, vigorous decomposition of 3-thiolene 1,1-dioxide begins. Since the hydrogenation of 3-thiolene 1,1-dioxide is an exothermic reaction (with a heat of 113 kJ mol^{-1}), inadequate removal of the heat evolved may promote the decomposition of the substrate. The primary products of the decomposition of 3-thiolene 1,1-dioxide under hydrogenation conditions react with formation of polysulfones and 3-alkoxythiolane 1,1-dioxides.

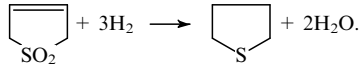
$$SO_2 + C_4H_6 \longrightarrow \left(—SO_2—C_4H_6—\right)_x,$$



Divalent sulfur compounds, which are poisons for metallic catalysts may also be formed.

$$SO_2 + 3H_2 = H_2S + 2H_2O,$$

$$C_4H_6 + H_2 + H_2S = C_4H_9SH,$$



When the degree of poisoning of catalysts is estimated, it is very important to select correctly the criteria of resistance to sulfur. There is no unanimous view concerning this question. In order to compare catalysts, the reactions of the sulfur-containing raw material are frequently carried out under standard conditions (at a definite temperature, pressure, contact time, and concentration of the poison)[100] and the resistance of the catalyst to sulfur is inferred from the yield of the product or from the degree of conversion of the substrate after a specific time interval. Such a measure of resistance to sulfur cannot be regarded as correct, its unsuitability being particularly evident when catalysts with different surface areas are compared.

Since the reaction rate referred to unit surface of the active component, measured in the kinetic region, is the generally accepted characteristic of catalytic activity, in determining the resistance of catalysts to sulfur it is useful to estimate the change in specific activity under the influence of poisons. In order to determine the resistance to sulfur, in the genenal case it is sufficient to determine the amount of poison in the reaction mixture for

which the specific activity falls to a specified value. The main cause of the deactivation of the catalyst is frequently the decrease in the number of accessible active centres as a consequence of the chemisorption of the poison on them. At a constant temperature, the rate of adsorption and the amount of the adsorbed substance depend only on the concentration of the poison in the reaction mixture. In this case, it is more correct to consider the change in the specific activity of the catalyst as a function of the concentration of the poison in solution and not as a function of the poison: catalyst ratio frequently employed. It has been established [79, 100] that the specific rate of hydrogenation of 3-thiolene 1,1-dioxide in isopropyl alcohol on the 1% Pd/Al_2O_3 catalyst (20 °C, $P = 0.1$ MPa, $c = 0.127$ M) remains constant ($W = 0.2$ mmol min^{-1} m^{-2} Pd) with the concentration of the poison (thiolane) remaining unchanged at 0.5×10^{-3} M and for different ratios (0.5–4) of the number of moles of the poison to the number of gram-atoms of palladium. If this ratio is kept constant at unity and the concentration of thiolane is increased from 0.1×10^{-3} to 1.75×10^{-3} M, then the specific rate of hydrogenation of 3-thiolene 1,1-dioxide falls by an order of magnitude (from 1.2 to 0.15 mmol h^{-1} m^{-2} Pd).

When the specific surface of the catalyst remains constant as a function of time, it is useful to measure not the specific activity of the catalyst but the productivity or degree of conversion of the substrate (if it is less than 100%) in order to obtain an approximate estimate of the resistance to sulfur. The resistance of catalysts to poisoning has been determined in the kinetic region.[18, 42, 66, 79] For this purpose, the activities of the catalyst in reactions using the pure starting material and the starting material to which a definite amount of poison had been added were compared. A fresh portion of the catalyst was taken for each experiment and the reaction was carried out during the same time interval. In order to determine the resistance of catalysts in the hydrogenation of 3-thiolene 1,1-dioxide to the poisons present in the initial solution and those generated in the course of the process, the experiments were performed for the same catalyst sample, several portions of the substrate being introduced successively into the hydrogenated solution, the composition of which was kept constant. The concentration of the poison or the amount of thiolane 1,1-dioxide for which different catalysts are deactivated to the same level was assumed to be a measure of the resistance to sulfur. This level was as a rule characterised by the ratio W/W_0, where W is the current reaction rate and W_0 is its initial value.

In the initial stage, the ratio W/W_0 decreases almost linearly as the concentration of the poison introduced or the amount of thiolane 1,1-dioxide formed on hydrogenation increases. Afterwards, the rate of change of the activity decreases and it is finally stabilised at a constant, lower than initial, level. The nonlinear decrease in activity is caused by the inhomogeneity of the catalyst surface and the attainment of the limiting level is due to the establishment of a new stationary state of the catalyst under the influence of the reaction medium. This may be associated with a change in the nature of the active component, for example with the conversion of the metal into the sulfide or with the appearance of steric hindrance in the interaction of the sulfur-containing poison with the active centre of the catalyst.

The results of studies of the resistance of various metals to sulfur in the hydrogenation of 3-thiolene 1,1-dioxide are described below.

Iridium, osmium, ruthenium, and platinum. In the hydrogenation of 3-thiolene 1,1-dioxide, iridium, osmium, ruthenium,and platinum blacks as well as the same metals deposited on γ-Al_2O_3 are unstable and their activity diminishes as the reaction proceeds.[42, 93] The complete deactivation of 1 g of the catalyst occurs after the formation of between 8 and 42 mmol of thiolane 1,1-dioxide (Table 2).

It has been established for the Ru/Al_2O_3 catalyst that the resistance to sulfur is independent of the hydrogen pressure in the range 0.1–10 MPa and amounts to ~ 40 mmol g^{-1}. The resistance of platinum to sulfur is influenced by the acidity of the hydrogenated solution. Thus, in the hydrogenation of the second portion of 3-thiolene 1,1-dioxide, the initial activity of the same platinum sample decreases by a factor of 3 in a neutral solution and by a factor of 1.2 in a hydrochloric acid solution.[47]

The specific resistances of ruthenium, iridium, and platinum blacks per unit surface are the same as the resistances of these metals deposited on γ-Al_2O_3 (Table 2).

Sulfur dioxide and hydrogen sulfide are strong poisons for ruthenium and platinum.[42] For complete deactivation of these metals, the hydrogenated solution should contain 0.05×10^{-3} and 0.7×10^{-3} M of hydrogen sulfide respectively or $\sim 0.14 \times 10^{-3}$ M of sulfur dioxide.

Rhodium. Metallic rhodium is relatively stable in the course of the hydrogenation of 3-thiolene 1,1-dioxide: the complete deactivation of 1 g of rhodium black occurs only after the formation of 1330 mmol of thiolane 1,1-dioxide.[42] The resistance to sulfur referred to unit mass of the catalyst is higher the higher the degree of dispersion of rhodium and the resistance calculated per m^2 of the metal is independent of the degree of dispersion of the latter (Table 3).

Rhodium is deactivated by sulfur dioxide.[42, 48, 49] When the hydrogenated solution contains SO_2 at a concentration of 0.08×10^{-3} M, the activity of rhodium black decreases by a factor of 2 and at $[SO_2] = 0.125 \times 10^{-3}$ M the catalyst loses its activity altogether. Divalent sulfur compounds are also poisons for rhodium. For example, when H_2S is introduced at concentrations of 0.6×10^{-3} and 1×10^{-3} M, the activity of rhodium black decreases by 50% and 100% respectively. Treatment of rhodium black with gaseous sulfur dioxide and hydrogen sulfide (20 °C, $P = 0.1$ MPa, $t = 5$ min) reduces sharply its initial activity in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, $P = 5$ MPa, $c = 0.4$ M). Whereas the rate of formation of thiolane 1,1-dioxide on fresh rhodium is 52.5 mol h^{-1} g^{-1}, after treatment with gaseous SO_2 and H_2S it decreases to 0.14 and 0.06 mol h^{-1} g^{-1} respectively.[49] When the rhodium catalyst is treated with hydrogen sulfide, its temperature rises to 200 °C, but this effect is absent in the interaction of rhodium with sulfur dioxide. It has been suggested that sulfur dioxide is adsorbed on rhodium associatively, whereas hydrogen sulfide is adsorbed dissociatively.[42, 49]

The deactivated rhodium catalyst cannot be regenerated by washing with water, acetone, isopropyl alcohol and hydrogen peroxide with subsequent heat treatment in an inert medium or in hydrogen at 100–300 °C. Oxidative treatment of the deactivated rhodium catalyst at 50–300 °C also fails. One of the causes of such failure may be the oxidation of metallic rhodium to the oxide Rh_2O_3, which does not exhibit an activity in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, $P = 5$ MPa, $c = 0.4$ M, $g_{ct} = 1.8$ g $litre^{-1}$, $t = 1$ min). After its reduction with hydrogen at 300 °C for 2 h, the specific surface diminishes from 162 to 9.5 m^2 g^{-1} and the metallic rhodium formed greatly accelerates the hydrogenation of 3-thiolene 1,1-dioxide (specific activity 230 mol h^{-1} g^{-1}).[48, 93] The XPA spectrum of rhodium black treated with air at 100–500 °C shows lines characteristic of metallic rhodium (2.20, 1.90, 1.345, and 1.146 Å). Rh_2O_3 lines (3.68, 3.62, 2.722, and 2.623 Å) appear in the spectrum of specimens oxidised at 400–500 °C.[82]

The oxidation-reduction regeneration of rhodium catalysts may be difficult because of the high stability of the surface compounds, the decomposition of which requires severe conditions, in particular the use of high temperatures, which promotes the sintering of the metal. Thus, when the Rh/Al_2O_3 catalyst treated with hydrogen sulfide or sulfur dioxide at 20 °C as well as authentic rhodium sulfide and sulfate deposited on γ-Al_2O_3 are heated in air, the evolution of sulfur dioxide does not begin until 600 °C.

Nickel. The hydrogenation of 3-thiolene 1,1-dioxide has been studied in detail [57] in the kinetic region on Raney nickel obtained by leaching an alloy containing 53.2 mass % of Al, 44.1 mass % of Ni, and 2.7 mass % of Ti. With increase in contact time, the

reaction rate constant fell (20 °C, $P = 4-5$ MPa, $c = 0.37$ M). This may be a consequence of the deactivation of the catalyst. Indeed on successive hydrogenation of several portions of 3-thiolene 1,1-dioxide for a constant composition of the hydrogenated solution, the rate of reaction fell with increase in the amount of thiolane 1,1-dioxide formed.

The rate of hydrogenation is influenced by the composition of the solvent: in thiolane 1,1-dioxide and in the mixture of isopropyl alcohol with 10 mass % – 15 mass % of thiolane 1,1-dioxide, the reaction rates differ almost by an order of magnitude (0.83 and 5.42 mol h^{-1} g^{-1} respectively). However, the stability of the catalyst is independent of the nature of the solvent and is determined solely by the amount of hydrogenated 3-thiolene 1,1-dioxide. The stability of the catalyst is influenced by the hydrogenation temperature. Thus, when the reaction is carried out at 21 and 25 °C ($P = 5$ MPa, $c = 0.37$ M), the complete deactivation of 1 g of Raney nickel takes place after the formation of 133 and 75 mmol of thiolane 1,1-dioxide respectively.

The rate of hydrogenation is influenced also by the content of the sulfur dioxide impurity in the solution: at SO_2 concentrations of 0.2×10^{-3} and 40×10^{-3} M, the reaction rates are 0.83 and 0.3 mol h^{-1} g^{-1} respectively. The absence of a direct proportionality between the rate and the SO_2 concentration is probably due to the additional formation of sulfur dioxide during the reaction. The linear decrease in the activity of nickel with increase in the amount of hydrogenated 3-thiolene 1,1-dioxide and the independence of the activation energy of the degree of deactivation of the catalyst ($E = 25 \pm 8$ kJ mol^{-1}) permitted the conclusion that the deactivation of nickel is induced by the decrease in the fraction of the working active surface of the catalyst.[57]

At the end of the hydrogenation of 3-thiolene 1,1-dioxide, the nickel potential is found to be below the hydrogen potential before the reaction, which may be a consequence of the partial dehydrogenation of the surface. The decrease in the stability of the catalysts as a consequence of dehydrogenation may be reduced by carrying out the process in the external diffusion region (in relation to the compound hydrogenated).[101] However, the stability of the 50% Ni/Cr_2O_3 nickel catalyst is virtually independent of the region in which the reaction is carried out.[46, 63, 69] Thus in the kinetic region (30 °C, $P = 2$ MPa, $c = 0.4$ M, solution in thiolane 1,1-dioxide), in the external diffusion region in relation to 3-thiolene 1,1-dioxide (35 °C, $P = 5$ MPa, $c = 1$ M), and in the external diffusion region in relation to hydrogen (20 °C, $P = 0.1$ MPa, $c = 0.2$ M, solution in isopropyl alcohol), complete deactivation occurred after the formation of 167, 150, and 130 mmol of thiolane 1,1-dioxide per gram of the catalyst respectively.

The degree of dehydrogenation can also be diminished by increasing the strength of the bond between hydrogen and the surface, for example by increasing the pH of the medium.[39] Thus, in the hydrogenation of 3-thiolene 1,1-dioxide on the nickel-chromium catalyst in solution in isopropyl alcohol at pH 10.4, the anodic shift of the catalyst potential is smaller by 100 mV than at pH 6.5. This indicates a strengthening of the bond between hydrogen and the surface at the high pH. However, this factor does not affect the stability of the catalyst, its deactivation occurring after the formation of 150 – 170 mmol of thiolane 1,1-dioxide per gram of the catalyst.

The strengthening of the bond between hydrogen and the surface of the nickel-chromium catalyst is promoted by the addition of 1 mass % of platinum.[65, 67, 68] This is indicated by the results of the measurement of the catalyst potentials. After the introduction of 3-thiolene 1,1-dioxide into a neutral solution (20 °C, $P = 0.1$ MPa) the shift of the Ni/Cr_2O_3 potential was 250 – 300 mV and that of the $(Ni + Pt)/Cr_2O_3$ potential was 100 mV. The initial activity of the nickel-chromium catalyst does not change after the addition of 0.1 mass % – 4.0 mass % of platinum ($W = 33-35$ mol h^{-1} g^{-1}). This is explained by the fact that the hydrogenation reaction is limited by the activation of the substrate.[17] The Pt/Cr_2O_3 catalyst exhibits an extremely low activity and a low stability in the hydrogenation of 3-thiolene 1,1-dioxide. On the other hand, the $(Ni + Pt)/Cr_2O_3$ specimen is much more stable than the unpromoted specimen. Thus Ni/Cr_2O_3 was fully deactivated after the formation on it of 150 mmol of thiolane 1,1-dioxide per gram of the catalyst, while the deactivation of specimens containing in addition 1 mass % and 4 mass % of platinum required the formation of 260 and 420 mmol g^{-1} of thiolane 1,1-dioxide. The increase in the stability of the $(Ni + Pt)/Cr_2O_3$ system is probably due to the decrease in the degree of dehydrogenation of the surface as a consequence of the strengthening of the bond between hydrogen and the catalyst. This reduces the rate of interaction of the poison in the starting material with the catalyst and, what is most important, hinders the dissociative adsorption of 3-thiolene 1,1-dioxide with formation of contact poisons.

In the hydrogenation of 3-thiolene 1,1-dioxide to thiolane 1,1-dioxide in isopropyl alcohol, the resistance of Raney nickel to sulfur may be increased by modifying it by adding certain metals.[59] The stability of modified Raney nickel depends on the Ni : Al ratio in the alloy and on the method used to introduce the additives (in the fusion stage or during the leaching process). In the modification of Raney nickel by the addition of 0.1 mass % – 1 - mass % of copper, cobalt, chromium, or platinum in the leaching stage, the stability of the catalyst increases by a factor of only 1.1 – 1.6, whilst after the addition of 0.1 mass % – 2 mass % of vanadium or molybdenum the increase is by a factor of 2 – 3. The addition of molybdenum (1 mass % – 12.5 mass %), vanadium (4.7 mass % – 14.8 mass %), and zirconium or niobium (1 mass %) to nickel in the fusion stage leads to the formation of a catalyst more stable by a factor of 2 – 7 than unpromoted Raney nickel (Table 4).

The hydrogenation of 3-thiolene 1,1-dioxide on the nickel catalyst may be complicated by the occurrence of side reactions involving the formation of buta-1,3-diene, sulfur dioxide, butanethiol, and hydrogen sulfide (see above). The activity of the nickel-chromium catalyst in the hydrogenation of 3-thiolene 1,1-dioxide in the kinetic region in the presence of these substances diminishes (30 °C, $P = 0.1$ MPa, $c = 0.85$ M, solution in thiolane 1,1-dioxide).[66]

Thiolane is a powerful poison for the nickel-chromium catalyst: the initial rate of hydrogenation (16 mmol h^{-1} g^{-1}) decreased by a factor of approximately 6 after the introduction of thiolane at a concentration of 4×10^{-3} M into the hydrogenated solution. However, a further increase in the thiolane concentration does not alter the rate of hydrogenation. The existence of a limit to poisoning by thiolane can be explained by the fact that, in the interaction with the relatively large thiolane molecules (effective size ~ 60 Å), a proportion of the nickel atoms are protected. Taking into account the size of the thiolane molecule and the Ni – Ni interatomic distance, one may claim that the maximum degree of surface coverage by thiolane does not exceed 50%.[102] The limiting capacity of the nickel-chromium catalyst with respect to thiolane, determined from the adsorption of the latter from solutions in xylene, is 0.17 mmol per gram of the catalyst and is attained at a thiolane concentration of 16×10^{-3} M. In the presence of this content of the poison, the catalyst nevertheless still possesses some activity. Part of the thiolane is probably adsorbed on the surface sites which are not involved in hydrogenation.

Butanethiol at a concentration of $(1-2) \times 10^{-3}$ M hardly affects the activity of the nickel-chromium catalyst presaturated with hydrogen. The rate of hydrogenation on the catalyst which has not been saturated with hydrogen initially diminishes after the addition of butanethiol at a concentration of $\sim 1 \times 10^{-3}$ M, but, as the reaction proceeds, it increases again and becomes the same as in the absence of the additive. It has been stated [103] that nickel is reversibly poisoned by phenylmethanethiol. The observed effect can be accounted for by the fact that the thiol is weakly adsorbed on the surface, forming either a Ni – S bond, which is weakened owing to the reduced electron-donating capacity of the sulfur in the thiol,[40] or a weak Ni – C bond.[104] The thiol weakly bound to

the surface is gradually displaced into the solution by 3-thiolene 1,1-dioxide or hydrogen.[66]

The hydrogen sulfide present in the hydrogenated solution at a low concentration (up to 0.2×10^{-3} M) increases the rate of hydrogenation of 3-thiolene 1,1-dioxide on the nickel-chromium catalyst by a factor of 1.5. However, at a higher concentration $(2.3-17) \times 10^{-3}$ M the rate of hydrogenation decreases by a factor of approximately 5.[66] Similar effects involving the promotion and poisoning of nickel by divalent sulfur compounds have been observed by Kinza *et al.*[105] They were explained by the fact that, as a consequence of the transfer of *p* electrons of the sulfur atom in hydrogen sulfide to the *d* band of nickel, the reactant–catalyst bond is loosened. At a low concentration of the sulfur compound, the optimum bond strength, most suitable for hydrogenation, is attained and this increases the rate of reaction. At a high hydrogen sulfide concentration in solution, the promotion effect is overlapped by the effect involving the blocking of the catalyst surface by the sulfur-containing poison and the rate of hydrogenation falls.

Sulfur dioxide is reduced on the nickel–chromium catalyst to hydrogen sulfide at a rate of 2 mmol h^{-1} g^{-1} {30 °C, $P = 0.1$ MPa, $g_{ct} = 50$ g^{-1} litre^{-1}, $[SO_2] = 9.4 \times 10^{-3}$ M}. When sulfur dioxide is introduced into the hydrogenated solution, the same effects are therefore observed as in the presence of hydrogen sulfide.[66]

Buta-1,3-diene at its concentration in solution of $(0.19-35) \times 10^{-3}$ M, increases by a factor of 2 the rate of hydrogenation of 3-thiolene 1,1-dioxide on the nickel-chromium catalyst. In the absence of 3-thiolene 1,1-dioxide, the hydrogenation of buta-1,3-diene is extremely slow and leads to the rapid deactivation of the catalyst, possibly as a consequence of polymerisation. However, the deactivation has been explained [66] by the interaction of the π electrons of the conjugated system with the *d* band of nickel *via* the mechanism proposed by Kinza *et al.*[105] At a concentration of $(35-208) \times 10^{-3}$ M, buta-1,3-diene induces a small decrease (by a factor of ~ 1.2) of the rate of hydrogenation of 3-thiolene 1,1-dioxide, probably owing to the formation of a butadiene film on the nickel surface or as a consequence of the displacement of part of the substrate from the catalyst by butadiene.

Thus the poisons for the nickel–chromium catalysts are thiolane, hydrogen sulfide, and sulfur dioxide, which can be arranged in the following sequence in terms of their toxicity (the concentration of the poison expressed in mmol litre^{-1} at which the rate of hydrogenation of 3-thiolene 1,1-dioxide decreases by a factor of 2):

$$SO_2\,(0.43) > \underset{S}{\square}\,(0.89) > H_2S\,(1.8).$$

For the complete poisoning of the nickel–chromium catalyst, the content of the poison in solution should be $(2.3-3.9) \times 10^{-3}$ M. The poisoning of the catalyst is apparently associated with the formation of the Ni—S bond. It was therefore concluded that the above poisons deactivate the same active centres of the catalyst.[66]

The introduction of certain compounds is recommended for the neutralisation of the sulfur dioxide present in the hydrogenated solution.[53, 106–112] The stability of Raney nickel in the hydrogenation of 3-thiolene 1,1-dioxide increases by a factor of 2–4 after the addition of hydrogen peroxide to a neutral or alkaline (pH < 8) solution.[111] The hydrogenation of 3-thiolene 1,1-dioxide on massive nickel was carried out in benzene, dioxane, alcohol, and thiolane 1,1-dioxide to which small amounts of the carbonates, hydroxides, and alkoxides of alkali metals or organic amines had been added.[53] According to the author's claim, this makes it possible to carry out the process at an elevated temperature and to increase the lifetime of the catalyst. In the presence of added sodium bisulfite or its mixture with sodium hydroxide, at a concentration of 0.5 mass %–2 mass %, the stability of Raney nickel increases: the additives increase the maximum yield of thiolane 1,1-dioxide (20 °C, $P = 0.1$ MPa, $c = 0.3-0.6$ M) from 55% to 85%. The modified nickel (30–40 °C, $P = 10$ MPa, $c = 1.4$ M, $t = 6.5-8$ h) also works more steadily in the hydrogenation of 3-thiolene 1,1-dioxide in isopropyl alcohol or in thiolane 1,1-dioxide and, its mixture with water (1 : 1) in the presence of 2 mass %–4 mass % of pyridine.[112] The maximum yield of thiolane 1,1-dioxide in the absence of additives was 87%–89%, whilst in the presence of pyridine it increased to 100%. 3-Thiolene 1,1-dioxide decomposes on the catalyst which has not been washed free of alkali and polymeric compounds, tentatively polyacrolein, are formed on the surface.[112]

However, Mashkina *et al.*[57] established that the introduction of additives which, according to other data,[106–112] are detoxifying agents in relation to the poisons formed during the process (primarily sulfur dioxide), does not allow an increase in the stability of Raney nickel. Thus, in the hydrogenation of 3-thiolene 1,1-dioxide to thiolane 1,1-dioxide in the kinetic region {20 °C, $P = 4$ MPa, $c = 0.28$ M, $[SO_2] = 39 \times 10^{-3}$ M}, the addition of hydrogen peroxide and sodium, potassium, or ammonium hydroxides did not prevent the poisoning effect of sulfur dioxide (Table 8).

In the successive hydrogenation in the kinetic region of several portions of thoroughly purified 3-thiolene 1,1-dioxide (sulfur dioxide concentration 0.14×10^{-3} M) under the conditions of a constant composition of the hydrogenated solution, 1 g of nickel was fully deactivated after the formation of 183 mmol of thiolane 1,1-dioxide. Nor did the stability of the catalyst change after the addition to the hydrogenated solution of sodium hydroxide, ethyl methyl ketone, ionol, or triethylamine, while the addition of sodium bisulfite and large amounts of ionol actually reduced the rate of hydrogenation of 3-thiolene 1,1-dioxide by a factor of 2–3. Under these conditions, the additives did not influence the initial activity of the catalyst (Table 8).

Table 8. The influence of the addition of certain substances on the hydrogenation of 3-thiolene 1,1-dioxide on Raney nickel in thiolane 1,1-dioxide in the presence of sulfur dioxide.[57]

Additive	Content of additive [a] (mass %)	Activity /mmol h^{-1} g^{-1}	Stability /mmol g^{-1}
$[SO_2]_0 = 0.2$ mass %			
None	—	300	
H_2O_2	0.26	308	
	0.90	200	
NaOH	0.54	366	
	1.47	350	
KOH	0.85	250	
NH_4OH	1.2	183	
NaOH + H_2O_2	14.1 + 4.1	583	
$[SO_2]_0 = 0.01$ mass %			
None	—	830	183
NaOH	0.5	833	100
$NaHSO_3$	2.1	664	50
$CH_3OC_2H_5$	1.3	830	250
Ionol	0.4	1000	192
	1.0	835	108
$(C_2H_5)_3N$	0.8	830	183

[a] Relative to 3-thiolene 1,1-dioxide.

The nickel catalyst deactivated by sulfur compounds is difficult to regenerate.[113, 114]

Palladium. Like other Group VIII metals, palladium is deactivated in the course of the hydrogenation of 3-thiolene 1,1-dioxide. On the 2% Pd/SiO_2 catalyst, the yield of thiolane 1,1-

dioxide falls from 100% to 80% after the formation of 250 mmol of the latter on 1 g of the catalyst (20 °C, $P = 7.8$ MPa, $c = 1.4$ M, space velocity 4.5 h).[115]

After the completion of the hydrogenation of one portion of 3-thiolene 1,1-dioxide on the 5% $Pd/BaSO_4$ catalyst (30 °C, $P = 0.1$ MPa, $c = 0.07$ M), the potential of the latter becomes less than the reversible hydrogen potential (630–640 mV), which indicates partial poisoning of the surface.[47] On repeated hydrogenation, the initial activity of the catalyst, amounting to 0.92 mol h^{-1} g^{-1}, decreases by a factor of 4. It was established that this is associated with the deactivation of the catalyst and not with the accumulation of the reaction product in solution.

At a low temperature (10–30 °C), the stability of palladium-containing catalysts is determined solely by the amount of hydrogenated 3-thiolene 1,1-dioxide and not by the rate of its conversion.[42,93] For this reason, changes in the hydrogen pressure, the nature of the solvent, and in the content of the substrate in the latter do not affect the stability of the catalyst. However, with increase in temperature, the stability falls at unchanged pressure and 3-thiolene 1,1-dioxide concentration. Thus the stabilities of the 5% Pd/Al_2O_3 catalyst at $P = 5$ MPa, $c = 0.4$ M, and temperatures of 20, 30, 50, 70, and 80 °C were respectively 1040, 808, 433, 30, and 8 mmol g^{-1}. This is associated with the increase in the rate of decomposition of 3-thiolene 1,1-dioxide as the temperature rises with formation of products which poison palladium.

The degree of deactivation of the palladium-containing catalyst in the hydrogenation of 3-thiolene 1,1-dioxide depends on the purity of the hydrogenated solution. Thus, when the sulfur dioxide contents were 0.014×10^{-3}, 0.029×10^{-3}, and 0.04×10^{-3} M, 1 g of the 5% Pd/Al_2O_3 catalyst was fully deactivated after the formation on the latter of 416, 833, and 1833 mmol of thiolane 1,1-dioxide respectively.[42]

An increase in the palladium content increases the stability of the catalyst. The nature of the carrier (aluminium oxide, aluminosilicate, silicon dioxide, activated charcoal) also exerts a definite influence. Palladium deposited on γ-Al_2O_3 (Table 5) is the most stable.[77,83,93] It was shown above that the nature of the carrier and the surface concentration of palladium influence the degree of dispersion and activity of the latter. It was found that the more accessible becomes the palladium surface the greater the increase not only in the activity but also in the stability of the catalyst. The factors which tend to increase the activity per unit mass of the catalyst (a large area of the carrier, a high palladium content, the addition of boron, manganese, or platinum group metals, activation of the catalyst by air, and the optimum preparation procedure) have a favourable effect also on the stability of the palladium-containing catalyst (Tables 5–7).

Thus an increase in the stability of the palladium catalyst is promoted by a decrease in the hydrogenation temperature, by an increase in the accessible surface of the metal, and by the thorough elimination of sulfur dioxide from 3-thiolene 1,1-dioxide. Nevertheless, this does not fully protect the catalyst against deactivation.

The deactivation of palladium-containing catalysts is caused by their poisoning by tetravalent and divalent sulfur compounds.

Sulfur dioxide is capable of interacting with palladium. After the treatment of palladium with gaseous SO_2 (20 °C, $P =$ 0.1 MPa, $t = 5$ min), the specimen contains 0.4 mass % of sulfur. Sulfur dioxide is adsorbed on palladium-containing catalysts (1 mass %–8 mass % of Pd on γ-Al_2O_3, AlSi, SiO_2, or C) from solution in isopropyl alcohol with added 10 mass % of thiolane 1,1-dioxide at a rate of 0.006–0.012 mmol h^{-1} m^{-2} Pd.[18,42] SO_2 is rapidly adsorbed on palladium films even at −80 °C. For surface coverages up to 0.8, dissociative chemisorption takes place, but part of the sulfur dioxide is adsorbed without decomposition. The fraction of the associatively adsorbed SO_2 increases with increase in the degree of surface coverage. Sulfur dioxide may be removed by evacuation.[116]

After the desorption of sulfur dioxide, the activity of the palladium catalyst in the hydrogenation of 3-thiolene 1,1-dioxide is restored to the previous level. The addition of sulfur dioxide to the 3-thiolene 1,1-dioxide solution diminishes the activity of palladium. It follows from the analysis of the poisoning isotherms[18,42] that, when the SO_2 content is 0.18×10^{-3} M, the rate of reaction diminishes by a factor of 2, while at its concentration of 0.28×10^{-3} M complete deactivation of the catalyst takes place (20 °C, $P = 5$ MPa, $c = 0.4$ M). The activity of the 5% Pd/Al_2O_2 catalyst with adsorbed sulfur dioxide in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, $P = 5$ MPa, $c = 0.4$ M) is 15 times smaller than that of the initial specimen (13.3 and 0.03 mol h^{-1} g^{-1} respectively).[18,42] The stability of the catalyst therefore depends greatly on the purity of 3-thiolene 1,1-dioxide. Sulfur dioxide is formed to some extent also in the hydrogenation of 3-thiolene 1,1-dioxide because of the ready dissociation of the latter.

It has been established[117] that sulfur dioxide, which is a powerful π-electron acceptor, forms a dative bond with the central metal atom of the complex catalyst as a result of electron transfer from the metal to the unoccupied orbital of sulfur. It may be that this is true also of the solid metallic catalyst. The ability of palladium on which sulfur dioxide has been adsorbed to activate hydrogen may be retained under these conditions. Thus palladium treated with sulfur dioxide at 20 °C adsorbs hydrogen, but its activity in the hydrogenation of 3-thiolene 1,1-dioxide reduced.[18,116] This is apparently induced by the decrease in the dative capacity of palladium, which hinders the formation of a π-olefin complex ensures the activation of the C=C bond of the sulfone.

In the hydrogenation of 3-thiolene 1,1-dioxide contaminated by sulfur dioxide, the palladium-containing catalyst is deactivated and cannot be regenerated either by washing with solvents (water, acetone, and isopropyl alcohol), or by oxidation with hydrogen peroxide, or by exposure to a stream of an inert gas at 200–300 °C. The regeneration is achieved only as a result of the reduction of the specimen with hydrogen at 300 °C for 6 h.[88]

In a hydrogen atmosphere, the sulfur dioxide adsorbed on palladium is reduced to hydrogen sulfide and the rate of hydrogenation is 0.3 mol min^{-1} g^{-1} {20 °C, $P = 0.1$ MPa, solution in isopropyl alcohol, $[SO_2] = 0.1$ M} and increases with increase in pressure. It was therefore concluded[22] that the change in the catalytic properties of palladium is associated with the effect on the latter by the hydrogen sulfide arising during the reduction of sulfur dioxide.

Hydrogen sulfide also readily interacts with palladium. When the palladium-containing catalyst is treated with gaseous H_2S (20 °C, $P = 0.1$ MPa, $t = 5$ min), the specimen heats up to 200 °C. After such treatment, the catalyst contains 5 mass % of sulfur.[42] The adsorption of hydrogen sulfide on palladium is irreversible. The rate of hydrogenation of 3-thiolene 1,1-dioxide on the sulfided specimen is 80 times lower than on the fresh catalyst: at 20 °C, $P = 5$ MPa, and $c = 0.4$ M, it is respectively 13.3 and 0.16 mol h^{-1} g^{-1}. The introduction of hydrogen sulfide into the solution also reduces the rate of formation of thiolane 1,1-dioxide; at $[H_2S] = 0.1 \times 10^{-3}$ M, the activity decreases by a factor of 2 and at $[H_2S] = 0.2 \times 10^{-3}$ M the catalyst is fully deactivated. The complete deactivation of catalysts of different composition requires ~ 0.05 mmol of hydrogen sulfide per m^2 of palladium.

In the interaction of hydrogen sulfide with metallic palladium, palladium sulfide is probably formed even at room temperature. Like other metal sulfides, it is appreciably less active than the metal itself (see below).

The regeneration of Pd/Al_2O_3 poisoned with hydrogen sulfide can be achieved only after its reduction with hydrogen at 300 °C for 6 h.

Organic compounds of divalent sulfur also deactivate metallic palladium. The influence of various divalent sulfur compounds on the activity of the 4.7% Pd/Al_2O_3 catalyst in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, $P = 5$ MPa, $c = 0.4$ M, $t = 0.5$–1 min) has been investigated.[118] It was found that the

stability of the catalyst, estimated as the amount of sulfur required for the complete deactivation of 1 g of the catalyst (α_S), depends on the structure of the sulfur compound. In terms of their toxicity in relation to the catalysts of the hydrogenation of 3-thiolene 1,1-dioxide, the compounds can be arranged in the following sequence corresponding to the changes in the electron-donating capacity of the sulfur entering into their composition (the values of α_S expressed in mg-atom g^{-1} are indicated in brackets):

R_2S (R = C_1-C_{10}),  (0.5–0.8) > $PhCH_2SEt$ (1.0) >

> PhSMe (1.2) > n-C_4H_9SH (2.2) > H_2S (2.7) >

> Ph_2S (4.4) >  (11.0).

A linear relation has been established between the Taft inductive constants and the toxicity of dialkyl sulfides, which indicates the formation of a surface donor–acceptor complex Pd←S<.[14, 118]

There exists the view that the resistance of metallic palladium to sulfur may increase when it is deposited on an acidic carrier (a zeolite or γ-Al_2O_3 with added boron) or on activated charcoal.[119–121] In order to elucidate the contribution of the carrier to the resistance of palladium to the poisoning effect of divalent sulfur compounds, a study has been made[79, 122] of the hydrogenation of 3-thiolene 1,1-dioxide with added $(0.05–5.0)\times10^{-3}$ M thiophene and thiolane on metallic palladium deposited on aluminium oxide, an aluminosilicate, silicon dioxide, activated charcoal, and zeolites. In order to avoid the distortion of the sulfur resistance data by effects due to the occurrence of side processes, the authors confined themselves to the measurement of the initial activity, which was inferred from the rate of absorption of hydrogen at the beginning of the stationary section on the kinetic curves (20 °C, P = 0.1 MPa, c = 0.127 M, conversion 25%–50%). The relative change from the initial rate of hydrogenation in the presence of the poison (W/W_0), determined from the poisoning isotherms, was adopted as the criterion of the resistance of the catalyst to sulfur. In the absence of the poison, the hydrogenation on all the catalysts investigated occurred at a high rate and with 100% yield of thiolane 1,1-dioxide. The rate of reaction remained constant up to the absorption of ~ 70% of the theoretically required amount of hydrogen and was independent of the size of the catalyst sample (g_{ct} = 0.5–2.5 g litre^{-1}). The catalysts differed as regards their activities referred to unit mass of the specimen, but the activities calculated per unit surface of the metal were approximately the same (Table 9) The introduction of thiophene and thiolane into the reaction mixture reduced the rate of hydrogenation, the fall being most marked at a poison concentration up to 0.2×10^{-3} M. At higher concentrations, the rate of decrease in the activity fell and at a poison concentration in excess of 2×10^{-3} M the catalyst was fully poisoned. At a concentration > 1.5×10^{-3} M the toxicity of thiolane is higher by a factor of 1.5–3.0 than that of thiophene, but at a lower concentration their toxicities are virtually the same.

Palladium black and palladium deposited in an amount of 1 mass % Al_2O_3, AlSi, SiO_2 or C have similar resistances to sulfur: a twofold decrease in activity occurs in all cases at a thiolane concentration of ~ 0.06×10^{-3} M, *i.e.* the nature of the carrier does not affect the stability of the catalyst. At a constant concentration of the poison, the values of W/W_0 for supported catalysts with different palladium contents are virtually the same and close to the corresponding value for palladium black. Since the specific surfaces of the test specimens differed by approximately one order of magnitude, one may conclude that the degree of dispersion of palladium does not affect the stability of the catalyst in relation to the poisoning effect of divalent sulfur compounds. experiments on the hydrogenation of 3-thiolene 1,1-dioxide with added thiolane showed that the 1% Pd/HNaY catalyst has a low activity (Table 9), but at a poison concentration of $(0.15–2.0)\times10^{-3}$ M the quantity W/W_0 on this specimen is approximately twice as high as on other supported palladium catalysts. This is associated with the partial adsorption of thiolane on the zeolite. However, the zeolite carrier does not fully protect metallic palladium against poisoning and, when thiolane is introduced into the solution at a concentration of 2.5×10^{-3} M, the ratio W/W_0 is only 3%.The different acidities of the palladium-zeolite catalyst containing 0.9 mass % – 7.8 mass % of sodium do not affect their resistance to sulfur. The acid centres of the zeolite framework influence the electronic state of palladium, but this is hardly reflected in its resistance to poisoning by divalent sulfur compounds. The results failed to confirm the hypothesis[119–121] that the deposition of palladium on an acid carrier or charcoal significantly protects it against poisoning by sulfur compounds.

Table 9. The resistance of various palladium-containing catalysts to sulfur in the hydrogenation of 3-thiolene 1,1-dioxide (20 °C, P = 0.1 MPa, c = 0.127 M).[79, 122]

Catalyst	S_{sp} /m^2 g^{-1} Pd	Rate of hydrogenation of pure substrate		[Poison][c]	W/W_0 (%)	
		see[a]	see[b]		thiolane	thiophene
Pd black	40	1.0	2.5	0.1	42	–
	40	1.0	2.5	0.24	20	–
0.1% Pd/Al_2O_3	380	17.4	4.9	0.24	14	22
0.5% Pd/Al_2O_3	300	14.7	5.2	0.78	8	12
1% Pd/Al_2O_3	260	10.2	4.2	0.24	18	24
	260	10.2	4.2	0.78	5	12
	260	10.2	4.2	0.05	53	46
	260	10.2	4.2	0.10	36	27
	260	10.2	4.2	0.15	27	26
	260	10.2	4.2	0.50	9	22
0.1% Pd/SiO_2	220	4.6	2.2	0.24	13	20
0.5% Pd/SiO_2	130	4.2	3.4	1.2	4	21
1% Pd/SiO_2	67	1.6	2.6	0.24	12	–
	67	1.6	2.6	1.2	4	7
0.2% Pd/AlSi	140	3.7	2.8	0.45	5	22
0.5% Pd/AlSi	65	2.3	3.7	1.2	4	10
1% Pd/AlSi	75	2.2	3.1	0.45	8	–
	75	2.2	3.1	1.2	3	19
1% Pd/C	165	5.8	3.7	0.5	8	21
5% Pd/C	84	2.4	3.1	1.2	5	9
1% Pd/NaHY:						
7.8% Na	–	0.5	–	0.15	66	–
1.5% Na	–	0.4	–	0.15	64	–
0.9% Na	–	0.5	–	0.15	57	72
	–	0.5	–	1.0	19	17

[a] Expressed in (mmol H_2) min^{-1} (g-atom Pd)$^{-1}$. [b] Expressed in (mmol H_2) min^{-1} m^{-2} Pd. [c] Expressed in mmol litre^{-1}.

Thus, during the hydrogenation of 3-thiolene 1,1-dioxide, metallic palladium is deactivated by various sulfur compounds. At a low temperature, the poisons in relation to palladium are sulfur dioxide as well as the hydrogen sulfide appearing when the latter is hydrogenated, while at a high temperature organic divalent sulfur compounds are also formed in addition during the process.

The poisoning of metallic palladium by sulfur-containing impurities may be diminished by introducing acid or alkaline additives into the hydrogenated solution.[123] Thus, in the hydrogenation of 2-thiolene 1,1-dioxide in a neutral solution in isopropyl alcohol (20 °C, P = 0.1 MPa, c = 0.127 M), the activity of the 2.5% Pd/Al_2O_3 catalyst decreases by a factor of 2 following the addition of thiolane at a concentration of 0.1×10^{-3} M. On

the other hand, in the presence of KOH at a concentration of $(0.25-2.5)\times10^{-3}$ M, the concentration of thiolane required to achieve this effect is $(0.6-1.25)\times10^{-3}$ M, *i.e.* the resistance of the catalyst to sulfur increases approximately by an order of magnitude. The strength of the bond between hydrogen and the surface probably increases in an alkaline medium and this hinders the chemisorption of thiolane on the active centres. The stability of the same catalyst in the hydrogenation of 2-thiolene 1,1-dioxide in isopropyl alcohol containing an admixture of sulfur dioxide increases by a factor of 2 after the acidification of the solution with hydrochloric acid (0.25×10^{-3} M). It may be that the catalytic poison is the hydrogen sulfide evolved on reduction of sulfur dioxide. Its interaction with palladium leads to the formation of palladium sulfide, while hydrochloric acid ruptures the Pd–S bond.[123] Alkali is introduced into the 3-thiolene 1,1-dioxide solution in order to neutralise sulfur dioxide.

The activity of the 2.5% Pd/Al_2O_3 catalyst in the presence of 0.1×10^{-3} M SO_2 in a neutral solution is lower by a factor of 2 than in the hydrogenation of pure 3-thiolene 1,1-dioxide. In the presence of $(0.25-2.5)\times10^{-3}$ M potassium hydroxide, the poisoning of the catalyst to the same level requires the introduction into the solution of 0.2–0.4 mmol of SO_2 per litre, *i.e.* the stability of the catalyst increases by a factor of 2–4.[123] In the hydrogenation of 3-thiolene 1,1-dioxide thoroughly freed from sulfur poisons, an increase in the basicity of the medium, for example by the introduction into the latter of KOH at a concentration of 2.25×10^{-3} M, also tends to increase the stability of palladium, since alkali neutralises the sulfur dioxide formed as a result of the partial decomposition of the substrate.[42] After the introduction of 0.5 mass % of potassium hydroxide into the 2% Pd/Al_2O_3 catalyst, its stability increases by a factor of two.[89,93] The stability of the 5% Pd/Al_2O_3 catalyst increases by a factor of 2.5–3.5 also when alkaline adsorbents (the NaY zeolite, Al_2O_3, or SiO_2, all containing 5 mass % of potassium) are added to the solution.[42,93] However, the activity of palladium-containing catalysts in a basic medium is lower than in a neutral medium. Thus the rate of hydrogenation of 3-thiolene 1,1-dioxide (20 °C $P = 5$ MPa, $c = 0.4$ M) on 4.5% Pd/Al_2O_3 in a neutral medium is 500 mol h^{-1} g^{-1}, while after the addition of 0.01 mass % NaOH it is 150 mol h^{-1} g^{-1}.[42]

A more detailed study confirmed[22,93] that the rate of hydrogenation of 2- and 3-thiolene 1,1-dioxides diminishes in alcoholic solutions (Table 10). At atmospheric pressure, the rate of hydrogenation in isopropyl alcohol {20 °C, $[KOH] = (0.1-10)\times10^{-3}$ M} and 1-butanol {20 °C, $[KOH] = (13-150)\times10^{-3}$ M} decreases in proportion to the concentration of potassium hydroxide raised to the power 0.5. If the reaction is carried out in isopropyl alcohol (to which 10% of thiolane 1,1-dioxide has been added) at an elevated hydrogen pressure (5 MPa), the above relation holds only for a NaOH concentration $< 2.3\times10^{-3}$ M while at a higher sodium hydroxide concentration the rate of decrease in the rate of hydrogenation of thiolene 1,1-dioxide diminishes.

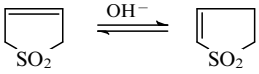
The decrease in the activity of metallic palladium in the hydrogenation of 3-thiolene 1,1-dioxide in an alkaline medium may be induced by various causes. In principle, one cannot rule out the possibility of the blocking of the active centres of the catalyst by the products of the alkaline cleavage of thiolene 1,1-dioxide or thiolane 1,1-dioxide, but such cleavage occurs at an appreciable rate only on refluxing in an aqueous alkaline medium.[124] The second cause may be the increase in the alkaline medium of the strength of the bond between hydrogen and palladium.[39] The hydrogenation of 3-thiolene 1,1-dioxide on metallic catalysts at atmospheric pressure is limited by the activation of hydrogen,[17] so that the strengthening of its bond with palladium may decrease the rate of reaction. With increase in pressure, the mechanism of the hydrogenation of 3-thiolene 1,1-dioxide changes and a strengthening of the bond between hydrogen and the surface therefore has a smaller effect on the activity of the catalyst.

Table 10. The influence of the concentration of alkali on the activity of the Pd/Al_2O_3 catalysts in the hydrogenation of 2- and 3-thiolene 1,1-dioxides.[22]

2.5% Pd/Al_2O_3, 20 °C, $P = 0.1$ MPa, $\mathring{a} = 0.4$ M, isopropyl alcohol		4% Pd/Al_2O_3, 20 °C, $P = 5$ MPa, $\mathring{a} = 0.4$ M, isopropyl alcohol		2% Pd/Al_2O_3, 70 °C, $P = 0.1$ MPa, $\mathring{a} = 0.13$ M, 1-butanol	
[KOH] [a]	$10^2 W$ [b]	[KOH] [a]	$10^2 W$ [b]	[KOH] [a]	$10^3 W$ [b]
0	125	0	1541	0	70
0.1	110	0 [c]	1667	2 [c]	59
0.25	98	0.3	1500	10 [c]	53
0.5	92	0.5 [c]	933	13	50
1.5	75	1.0	830	40	35
2.5	68	0.9 [c]	833	65	24
3.0	62	2.3	575	80 [c]	22
4.5	50	2.2 [c]	592	100	16
5.0	41	23	267	130	13
10.0	29	112	150	150	8

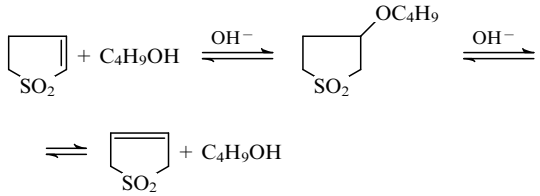
[a] Expressed in mmol $litre^{-1}$. [b] Expressed in mol h^{-1} g^{-1}. [c] Hydrogenation of 2-thiolene 1,1-dioxide. In the remaining cases, the hydrogenation of 3-thiolene 1,1-dioxide is meant.

The rate of hydrogenation of 3-thiolene 1,1-dioxide in an alkaline medium may also change owing to a transformation of the substrate unrelated to the catalytic hydrogenation. Thus the double bond in the 3-thiolene 1,1-dioxide ring may migrate under the influence of bases in alcoholic solutions with formation of 2-thiolene 1,1-dioxide.

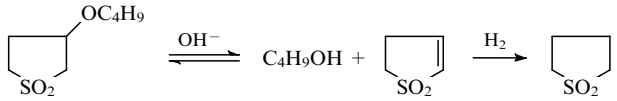


The isomerisation in the presence of an alkaline agent occurs even at room temperature and is accelerated on heating.[6] However, the conversion of 3-thiolene 1,1-dioxide into 2-thiolene 1,1-dioxide cannot be regarded as the cause of the decrease in the rate of formation of thiolane 1,1-dioxide in an alkaline medium in view of the following considerations. 2-Thiolene 1,1-dioxide is known to be hydrogenated at a high rate in a neutral medium.[1] Under comparable conditions, the rate of formation of thiolane 1,1-dioxide from 2-thiolene 1,1-dioxide is actually somewhat higher than the rate of its formation from 3-thiolene 1,1-dioxide. Thus, on the 2.5% Pd/Al_2O_3 catalyst in isopropyl alcohol, the rates of hydrogenation of 3- and 2-thiolene 1,1-dioxides are respectively 1.12 and 1.33 mol h^{-1} g^{-1} at 20 °C, $P = 0.1$ MPa, and $c = 0.4$ M and 3.8 and 4.5 mol h^{-1} g^{-1} at 20 °C, $P = 5$ MPa, and $c = 0.13$ M. Under the conditions of the hydrogenation of 2-thiolene 1,1-dioxide in a neutral medium at 20 °C, the palladium catalyst works more steadily than in the hydrogenation of 3-thiolene 1,1-dioxide: the initial rate of hydrogenation of 3-thiolene 1,1-dioxide on a 2.5% Pd/Al_2O_3 specimen, amounting to 12 mol h^{-1} g^{-1} decreases to 0.01 mol h^{-1} g^{-1} after the formation of 1000 mmol of thiolane 1,1-dioxide per gram of the catalyst, while 2-thiolene 1,1-dioxide is hydrogenated virtually at a constant rate of 12–14 mol h^{-1} g^{-1} (20 °C, $P = 5$ MPa, $c = 0.4$ M).[22] This is probably due to the fact that 2-thiolene 1,1-dioxide is predisposed to decompose with elimination of sulfur dioxide, which is a poison for palladium. In an alkaline medium, the rate of hydrogenation of 2-thiolene 1,1-dioxide on 2.5% Pd/Al_2O_3 decreases in proportion to the concentration of potassium hydroxide raised to the power 0.5, *i.e.* as happens in the hydrogenation of 3-thiolene 1,1-dioxide (Table 10). One may therefore conclude that the isomerisation of 3-thiolene 1,1-dioxide to 2-thiolene 1,1-dioxide does not decrease the rate of its hydrogenation in alkaline alcoholic solutions.

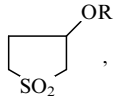
The isomerisation of 3-thiolene 1,1-dioxide to 2-thiolene 1,1-dioxide in primary and secondary alcohols is accompanied by the addition of the alcohol to the double bond activated by the electron-accepting sulfonyl group in the ring. This results in the formation of 3-alkoxythiolane 1,1-dioxides (sulfolanyl esters).[6] For example, 3-butoxythiolane 1,1-dioxide is formed in butanol.



The reaction is reversible, the content of 3-butoxythiolane 1,1-dioxide amounting to $94\% \pm 2\%$ in the presence of primary alcohols in the equilibrium mixture and to $88\% \pm 2\%$ in the presence of secondary alcohols. In an alkaline solution, 3-alkoxythiolane 1,1-dioxide may decompose with formation of 2-thiolene 1,1-dioxide. This reaction is also reversible.[6] However, if it is carried out under a hydrogen atmosphere in the presence of a hydrogenation catalyst, then the 2-thiolene 1,1-dioxide formed is hydrogenated and this shifts the equilibrium towards the formation of elimination products.



The occurrence of the above reactions results in the complete conversion of 3-thiolene 1,1-dioxide into thiolane 1,1-dioxide. The possibility of this transformation in the presence of 2.5% Pd/Al_2O_3 has been established in the hydrogenation of authentic 3-alkoxythiolane 1,1-dioxides having the general formula



where $R = C_1 - C_{12}$ {20–85 °C, $P = 0.1 - 5$ MPa, $c = 0.06 - 1.4$ M, [KOH] = 0–1.42 M}.[125] 3-Butoxythiolane 1,1-dioxide is the most reactive. Its hydrogenation takes place in alkaline alcoholic (isopropyl alcohol and *tert*-butyl alcohol), aqueous, and thiolane 1,1-dioxide solutions. In the absence of alkali the rate of reaction is very low. The quantitative yield of thiolane 1,1-dioxide is attained in an aqueous alkaline solution at an elevated temperature and a high content of alkali. The rate of formation of thiolane 1,1-dioxide in the presence of 2.5% Pd/Al_2O_3 from 3-butoxythiolane 1,1-dioxide is much lower than the rate of its formation from 3-thiolene 1,1-dioxide in a neutral medium (Table 11). With increase in temperature from 20 to 85 °C, the rate of formation of thiolane 1,1-dioxide from the ether increases, the activation energy being 25 ± 4 kJ mol^{-1}. The rate of reaction depends little on the hydrogen pressure: when it increases from 0.1 to 5 MPa, the rate increases by a factor of 1.3. In an aqueous alkaline solution, the rate of reaction of 3-butoxythiolane 1,1-dioxide initially increases in proportion to its concentration (up to 0.1 M) and then (at a concentration up to 1.5 M) remains constant. The rate of reaction is proportional to the concentration of potassium hydroxide raised to the power 0.5 {for [KOH] = 0.013–0.89 M}. Overall, the rate of formation of thiolane 1,1-dioxide from 3-butoxythiolane 1,1-dioxide is described by the equation

$$W = kc_1^n c_2^{0.5} P^{0.2},$$

where c_1 and c_2 are the concentrations of 3-butoxythiolane 1,1-dioxide and potassium hydroxide respectively, P is the hydrogen pressure, k is the reaction rate constant, and $n = 0$ or 1.

In the presence of alkali, the initial rates of hydrogenation of authentic 2-thiolene 1,1-dioxide and 3-butoxythiolane 1,1-dioxide are of the same order of magnitude. For example, at 85 °C, $P = 0.1$ MPa, $c = 0.127$ M, and [KOH] = 0.89 M, they are respectively 32 and 12 mmol h^{-1} g^{-1}. This observation and the fact that the rate of reaction depends little on the hydrogen pressure permit the conclusion that the formation of thiolane 1,1-dioxide from 3-butoxythiolane 1,1-dioxide is limited by the elimination of the alcohol and not by the reduction of the 2-thiolene 1,1-dioxide formed.[125]

In the hydrogenation of 2- and 3-thiolene 1,1-dioxides as well as 3-butoxythiolane 1,1-dioxide in alcoholic solutions, the rates of formation of thiolane 1,1-dioxide on the 2.5% Pd/Al_2O_3 catalyst are similar (Table 11). One may therefore postulate that the conversion of 3-thiolene 1,1-dioxide in alcoholic alkaline solutions proceeds *via* stages involving isomerisation and addition of the alcohol to the 2- and 3-thiolene 1,1-dioxides with formation of alkoxythiolane 1,1-dioxide and its subsequent hydrogenation to thiolane 1,1-dioxide. In order to attain an acceptable rate of formation of thiolane 1,1-dioxide, the hydrogenation must be carried out at an elevated temperature.

During the hydrogenation of 2- and 3-thiolene 1,1-dioxides and 3-butoxythiolane 1,1-dioxide on 2.5% Pd/Al_2O_3 at atmospheric pressure and a temperature in excess of 70 °C, the catalyst is

Table 11. Hydrogenation of 2- and 3-thiolene 1,1-dioxides and 3-butoxythiolane 1,1-dioxide on aluminopalladium catalysts at $P = 5$ MPa.[22]

Catalyst	Solvent	Compound hydrogenated	Content in initial mixture /M		T /°C	$10^3 W$ /mol h^{-1} g^{-1}
			Substrate	KOH		
2.5% Pd/Al_2O_3	Isopropyl alcohol	3-Thiolene 1,1-dioxide	0.4	0	20	11 670
		"	0.13	0	20	3750
		"	0.04	0	20	1250
		2-Thiolene 1,1-dioxide	0.4	0	20	12 840
		"	0.13	0	20	4500
		"	0.04	0	20	1500
	Butanol	3-Thiolene 1,1-dioxide	0.53	0	85	8.3
		"	0.53	0.45	87	12.0
		2-Thiolene 1,1-dioxide	0.60	0.45	87	12.5
		3-Butoxythiolane 1,1-dioxide	0.60	0.45	87	13.3
2.5% PdS/Al_2O_3	Butanol	3-Thiolene 1,1-dioxide	0.04	0	100	0.67
		"	0.04	0.45	100	1.0
		2-Thiolene 1,1-dioxide	0.04	0	100	0.83
		3-Butoxythiolane 1,1-dioxide	0.04	0.45	100	1.5

rapidly deactivated despite the high content of alkali in the solution. For example, at 70–85 °C, [KOH] = 0.45–0.89 M, and c = 0.13 M, the rate of reaction in an alkaline solution is a maximum in the first minute and then falls sharply (by an order of magnitude).[22, 125] The rate of formation of thiolane 1,1-dioxide from portions of the substrate introduced successively into the solution on the same catalyst sample (for a constant composition of the solution) does not remain constant. The amount of thiolane 1,1-dioxide formed on 1 g of the catalyst before the decrease in the initial activity by a factor of 20 is independent of the substrate concentration and amounts to $(2-5)\times10^{-3}$ M. At an elevated hydrogen pressure (5 MPa), the catalyst works more steadily: its initial activity does not decrease after the formation of ~ 400 mmol of thiolane 1,1-dioxide per gram of the catalyst.

The dependence of the stability of metallic palladium on the hydrogen pressure is determined by the ratio of the rates of isomerisation and hydrogenation of 2-thiolene 1,1-dioxide. At atmospheric pressure, the rate of hydrogenation is relatively low and 2-thiolene 1,1-dioxide isomerises to a large extent to 3-thiolene 1,1-dioxide, which is a source for the formation of catalytic poisons. At an elevated pressure, the contribution of the isomerisation process falls since the rate of hydrogenation increases markedly. The significance of the presence of 3-thiolene 1,1-dioxide in the hydrogenated solution for the deactivation of palladium has been confirmed also by experiments on hydrogenation at elevated temperatures, which promote its dissociation. Thus the rate of formation of thiolane 1,1-dioxide from 3-thiolene 1,1-dioxide on the 5% Pd/Al_2O_3 catalyst in isopropyl alcohol (P = 5 MPa, c = 0.53 M, conversion 70%) increases from 10 to 54 mol h^{-1} g^{-1} with increase in temperature from 8 to 50°C. At 70–85 °C, it falls sharply, reaching values from 0.4 to 0.01 mol h^{-1} g^{-1}, since the catalyst is fully deactivated.[93]

The sulfur dioxide evolved on decomposition of 3-thiolene 1,1-dioxide, is readily reduced in the presence of the palladium catalyst to hydrogen sulfide, which interacts with metallic palladium. Thermodynamic calculations indicate a high probability of the formation of palladium sulfide under these conditions. This process proceeds at a low temperature and accelerates when the latter is increased.[126] It has been established experimentally that metallic palladium is fully converted into palladium sulfide after treatment with hydrogen sulfide at 200 °C for 30 min.[19] On the other hand, thermodynamic calculations for the $PdS + H_2 \leftrightarrows Pd + H_2S$ system and experimental studies by the XPES and thermostimulated exoelectron emission methods[16, 127] indicate the possibility of the partial reduction of PdS to metallic palladium (and Pd_2S) at moderate temperatures. However, the reduction of palladium sulfide by hydrogen is much slower than the conversion of metallic palladium into the sulfide: at 200 °C, the degree of reduction is 2% and 83% after 1 and 10 h respectively.[19] One may therefore assume that the catalyst of the formation of thiolane 1,1-dioxide from thiolene 1,1-dioxides in an aIkaline medium at an elevated temperature and pressure is not metallic palladium but its sulfide.

In the presence of palladium sulfide (2.5% PdS/Al_2O_3) at an elevated temperature and a high hydrogen pressure, the hydrogenation of 2- and 3-thiolene 1,1-dioxides in a neutral medium and of 3-butoxythiolane 1,1-dioxide in an alkaline solution proceeds at the same rate as in the case where metallic palladium is employed as the catalyst (Table 11). In the hydrogenation of 3-thiolene 1,1-dioxide in an alcoholic alkaline solution on the 2.5% PdS/Al_2O_3 catalyst, the same behaviour is observed as in the hydrogenation of 2-thiolene 1,1-dioxide in a neutral medium:[22, 128] The rate of reaction is proportional to the substrate concentration and the hydrogen pressure. With increase in temperature from 80 to 110 °C, the yield of thiolane 1,1-dioxide obtained from 3-thiolene 1,1-dioxide on palladium sulfide in an alkaline medium initially increases from 78% to 90% {P = 5 MPa, c = 0.04 M, [KOH] = 0.45 M, g_{ct} = 25 g $litre^{-1}$}, but then falls to 58% at 135 °C and 22% at 200 °C. In the presence of Pd/Al_2O_3, the dependences of the rates of hydrogenation of 3-thiolene 1,1-dioxide and 3-butoxythiolane 1,1-dioxide on the concentration of alkali in the alcoholic solution are the same: the rate of reaction is proportional to the concentration of alkali raised to the power 0.5.[22, 125]

The similarity of the kinetics and of the rates of hydrogenation of 2- and 3-thiolene 1,1-dioxides and of 3-alkoxythiolane 1,1-dioxide in an alcoholic alkaline medium at an elevated temperature in the presence of Pd and PdS is a consequence of the similarity of the reaction mechanisms on catalysts of identical composition formed under the influence of the reaction medium. Thiolane 1,1-dioxide is formed from 3-thiolene 1,1-dioxide *via* stages involving its isomerisation to 2-thiolene 1,1-dioxide, the addition of the alcohol with formation of 3-alkoxythiolane 1,1-dioxide, and the reduction of the latter by hydrogen. The low activity of metallic palladium under the given conditions is due to the change in the nature of the active component — the conversion of Pd into PdS.

Thus the hydrogenation of 3-thiolene 1,1-dioxide on palladium-containing catalysts in the presence of added alkali has no advantage over the hydrogenation in a neutral medium on metallic palladium.

Metallic palladium catalysts deactivated in the hydrogenation of 3-thiolene 1,1-dioxide cannot be regenerated by washing them with solvents (water, alcohol, and acetone), by oxidation with hydrogen peroxide, or by exposure to a stream of nitrogen at 200–300 °C for 10 h. Treatment with hydrogen at 300 °C partially restores the activity of palladium (to the extent of ~ 80%), but full regeneration occurs only after additional treatment with air.[115]

The XPA spectra of palladium-containing specimens treated with air for 10 h at 100–400 °C exhibit only lines characteristic of metallic palladium (2.23, 1.94, 1.371, and 1.170 Å). In the specimen treated with air at 500 °C, the above lines vanish and those of PdO appear (3.046, 2.667, 2.664, and 2.153 Å).[82] For the activity of the catalyst, this is unimportant because palladium oxide is readily reduced to the metal even at 20 °C. The thermal stability of palladium compounds is low [129] and they are therefore relatively easily removed from the surface of the deactivated catalyst. On heating in air, the compounds weakly bound to palladium are desorbed, liberating part of the catalytically active surface. The substances strongly bound to the catalyst, for example a thiol and thiolane, may be oxidised to compounds which have a low toxicity or are nontoxic. Palladium sulfide, formed on interaction of palladium with hydrogen sulfide, is oxidised with evolution of sulfur dioxide, which reacts with palladium in an oxidising medium, affording a surface palladium sulfate. Palladium sulfide and sulfate, deposited on γ-Al_2O_3, are completely inactive in the hydrogenation of 3-thiolene 1,1-dioxide at 20 °C and P = 5 MPa. The activity of PdS/Al_2O_3 treated with hydrogen at 300 °C for 20 h is low, but after additional oxidation with air at 200–300 °C for 2 h the catalyst acquires the same activity as metallic palladium deposited on γ-Al_2O_3. A similar treatment of a $PdSO_4/Al_2O_3$ specimen proved ineffective. One cannot rule out the possibility, however, that the surface compounds formed on deactivation of palladium decompose more readily than the bulk-phase PdS and $PdSO_4$. Sulfur dioxide, water, and carbon dioxide are evolved on oxidative regeneration of palladium catalysts. They are formed on oxidation of the products of the decomposition of 3-thiolene 1,1-dioxide accumulated on the surface and also as a result of the conversion of the sulfided palladium and not as a result of the oxidation of adsorbed 3-thiolene 1,1-dioxide, alcohol, or thiolane 1,1-dioxide. In the oxidative regeneration of the deactivated Pd/Al_2O_3 catalyst, 5–7 times more sulfur and carbon dioxides are evolved than on treating with air a specimen wetted with a 10% solution of the substrate in a mixture of isopropyl alcohol and thiolane 1,1-dioxide. It has been established that the hydrogenation–regeneration cycles involving aluminopalladium catalysts can be repeated many times and that this does not alter the initial activity and duration of the interregeneration period.[88]

VI. Conclusion

As shown above, thiolane 1,1-dioxide can be synthesised by hydrogenating 2- and 3-thiolene 1,1-dioxides in the presence of various catalysts — metals, their complexes, and their sulfides. Group VIII metals have been investigated in greatest detail in this respect. The catalysts based on them exhibit a high activity and make it possible to obtain thiolane 1,1-dioxide in 100% yield by hydrogenation under mild conditions.

The most correct data on the relative activities and stabilities of the metals are obtained when thiolene 1,1-dioxides are hydrogenated in the absence of the distorting influence of mass-transfer processes and in estimating the catalytic properties account is taken of the specific surface of the active component. In terms of their activities in the hydrogenation of 3-thiolene 1,1-dioxide, the massive metals can be arranged in the sequence [42]

$$Rh > Pd > Pt > Ir > Ru > Ni\,.$$

The activities of iridium, ruthenium, and nickel per gram of the metal are approximately the same. Platinum is 6.5 times more active than the above metals and palladium and rhodium are 70 and 280 times more active respectively. When the activities are calculated per m^2 of the metal surface, the difference is more significant: nickel is the least active; the activities of ruthenium,iridium, and platinum exceed that of nickel by 1–2 orders of magnitude, and rhodium and palladium are more active by 3 orders of magnitude (Table 12). The activity series presented for the metals is close to the series established in the hydrogenation of other unsaturated compounds, for example cinnamic acid.[39] In all the hydrogenation reactions, a correlation is observed between the activities of the metals and their properties such as the criterion indicating the extent to which the *d* shell is unfilled, the electron work function, the energy of the bond between hydrogen and the metal, the heat of sublimation, and the crystal lattice parameters. This is explained by the fact that the electronic structure affects the hydrogenating activity of the metal.

The mechanisms of the hydrogenation of 3-thiolene 1,1-dioxide on various Group VIII metals are similar, so that identical kinetics are observed. At a constant 3-thiolene 1,1-dioxide concentration, the rate of hydrogenation is proportional to the hydrogen pressure at P up to 2 MPa and, when the latter is increased further, the rate remains unchanged. At a constant hydrogen pressure, the rate of reaction is proportional to the concentration of 3-thiolene 1,1-dioxide up to $c > 0.1$ M, remaining constant at $c \approx 0.1$ M. The transition from the first to the zero reaction order is associated with the change in the rate-limiting stage as a function of the degree of surface coverage of the catalyst by the reactants, which depends in its turn on the hydrogenation conditions.

Table 12. Comparison of the activities and resistances to sulfur of Group VIII metals in the hydrogenation of 3-thiolene 1,1-dioxide in isopropyl alcohol to which 10% of thiolane 1,1-dioxide has been added at 20 °C, $P = 5$ MPa, and $c = 0.4$ M (according to the data of Mashkina *et al.*[42]).

Metal	Activity [a] /mol h^{-1} g^{-1}	Specific stability [b] /mmol g^{-1}	Specific catalytic stability [b] /mmol g^{-1}	
			in the presence of SO_2	in the presence of H_2S
Rh	1836 (306)	1330 (225)	0.14 (0.023)	0.78 (0.13)
Pd	466 (92)	423 (83)	0.10 (0.020)	0.26 (0.05)
Pt	42 (19)	44 (20)	0.08 (0.035)	0.20 (0.09)
Ir	8 (2)	28 (7)	–	–
Ru	8 (1)	24 (3)	0.07 (0.009)	0.10 (0.012)
Ni	7 (0.1)	140 (2)	1.70 (0.025)	0.15 (0.002)

[a] The activity calculated per m^2 of the metal (mol h^{-1} m^{-2}) is given in brackets. [b] The stability of the catalyst calculated per m^2 of the metal (mmol m^{-2}) is given in brackets.

Group VIII metals are all sensitive to the addition of substances competing with the reactants for adsorption on the catalyst: complete deactivation occurs when less than 0.14 mmol of SO_2 or H_2S per m^2 of the metal is introduced into the solution (Table 12). In terms of the specific stability in the hydrogenation of 3-thiolene 1,1-dioxide, determined from the amount of thiolane 1,1-dioxide formed on 1 m^2 of the metal up to the complete deactivation of the catalyst, the Group VIII metals can be arranged in the same sequence as that based on the specific catalytic activity. Thus, the more active the metal the greater its stability (Table 12). A similar behaviour has been found also for supported catalysts: the factors ensuring an increase in activity promote also an increase in the resistance to sulfur. The causes of the existence of a direct relation between the activities and stabilities of the catalysts have been explained in a number of studies.[22, 93, 100] The stability of the catalyst (Y) depends on the ratio of the rates of hydrogenation of 3-thiolene 1,1-dioxide (W_h) and deactivation of the specimen (W_d). The latter is associated with the amount of poison present in the substrate (c_p), the rate of formation of the poison (W_p), and the rate of its adsorption (W_{ads}).

$$Y = \frac{W_h}{W_d} = \frac{W_h}{c_p W_p W_{ads}}\,.$$

The content of sulfur dioxide in solution is determined mainly by the purity of 3-thiolene 1,1-dioxide and the reaction temperature but not the nature of the catalyst. For the same degree of purification of the substrate and for the reaction carried out under relatively low-temperature conditions, the concentrations c_p are approximately the same. The rates W_p on different metals are also similar. The rates of adsorption of SO_2 on catalysts containing 1 mass % – 8 mass % of palladium on γ-Al_2O_3, SiO_2, AlSi, or charcoal, calculated per m^2 of palladium, are of the same of magnitude (0.4 – 0.8 mg h^{-1}). Therefore the more active the catalyst in the hydrogenation of 3-thiolene 1,1-dioxide the more stable its operation in this process.

Complexes of Group VIII metals have specific activities in the reactions considered which are not inferior to those of the metals themselves or are actually superior to them. In many instances the binding of the metal in a complex increases the resistance of the catalyst to sulfur. For example, the heterogenised palladium complexes are 3–50 times more stable and the homogeneous platinum complex is an order of magnitude more stable than the corresponding metals.[32, 35] However, the poisoning of the complexes by compounds of divalent and tetravalent sulfur cannot as yet be fully prevented. In the hydrogenation of 3-thiolene 1,1-dioxide, the complexes undergo a change in their initial structure or are fully decomposed. The possibility of their regeneration has not been investigated, but one may predict the appearance of a number of difficulties in the application of such a procedure.

Transition metal sulfides accelerate the hydrogenation of 2- and 3-thiolene 1,1-dioxides at an elevated temperature and pressure. Rhodium and palladium sulfides exhibit, like the metals themselves, a much higher activity than nickel sulfide; rhenium hemisulfide (Re_2S_7) also exhibits a high activity. However, the specific activities of all the metal sulfides investigated are lower by 2–3 orders of magnitude than those of Group VIII metals. Their advantage consists in the lack of sensitivity to sulfur compounds. However, the stability of the sulfides in the real reaction involving the hydrogenation of thiolene 1,1-dioxides has been very little investigated and one cannot rule out the possibility that the metal sulfides, exhibiting an activity under relatively severe conditions, will also be deactivated by the ring cleavage products condensing on the surface in the form of polymeric deposits. There is virtually no information about the regeneration of such deactivated catalysts.

The catalysts are more stable in the hydrogenation of 2-thiolene 1,1-dioxide. However, this substrate is less readily available than 3-thiolene 1,1-dioxide, from which it is obtained by its

isomerisation. This reaction is reversible and the content of 2-thiolene 1,1-dioxide in the equilibrium mixture is 50% – 60% and, when the product is isolated from the mixture by heating, 3-thiolene 1,1-dioxide decomposes fully. In the hydrogenation of 2-thiolene 1,1-dioxide, the yield of thiolane 1,1-dioxide relative to the more readily available 3-thiolene 1,1-dioxide does not exceed 60%. More rational ways of synthesising 2-thiolene 1,1-dioxide have not so far been found and it still remains more useful to obtain thiolane 1,1-dioxide by hydrogenating 3-thiolene 1,1-dioxide.

In practice, it is preferable to use Group VIII metals, which exhibit a high activity under mild conditions, as catalysts for the hydrogenation of 3-thiolene 1,1-dioxide. Rhodium is more active and stable than palladium, but the latter is less scarce, is cheaper, and is more readily regenerated. It is useful to employ catalysts on a carrier, since the supported metal is more highly dispersed and the catalyst itself exhibits an enhanced thermal stability. In terms of activity per unit surface, palladium is superior by 2 – 3 orders of magnitude to nickel. However, when a supported nickel catalyst with a high metal content, for example 50 mass % of Ni on Cr_2O_3 or SiO_2 or Raney nickel, is used, it is possible to attain a relatively high productivity and stability per unit mass of the catalyst. A serious disadvantage of nickel catalysts is their high sensitivity to sulfur-containing poisons and the lack of readily available regeneration methods.

As a result of systematic studies at the Institute of Catalysis of the Siberian Division of the Russian Academy of Sciences, catalysts have been proposed for the hydrogenation of 3-thiolene 1,1-dioxide to thiolane 1,1-dioxide — the industrial nickel – chromium catalyst and the palladium-containing IK-71-1 catalyst — and the optimum process conditions have been determined.[64, 69, 75]

The process is carried out on scaled up apparatus at a temperature below 25 °C and a pressure of 2 – 5 MPa. After the yield of thiolane 1,1-dioxide has fallen from 100% to 98% (600 h), the IK-71-1 catalyst is regenerated. High-quality thiolane 1,1-dioxide has been produced in this way on the experimental plant of the Salavat Petrochemical Group.[130]

Metallic catalysts, which are traditionally employed in low-temperature hydrogenation processes, suffer from significant disadvantages, the main one being their high sensitivity to poisoning by sulfur compounds in the synthesis of thiolane 1,1-dioxide. Because of this, the starting material must be thoroughly freed from sulfur, the process must be carried out under rigorously controlled conditions, and the catalyst must be regenerated periodically.

Taking into account the growing need for thiolane 1,1-dioxide, which is finding practical application on an increasing scale, it is necessary to intensify the research on the catalytic liquid-phase hydrogenation of thiolene 1,1-dioxides. The principal aspect of such research involves the creation of sulfur-resistant catalytic systems based on a detailed investigation of the hydrogenation and deactivation mechanisms. In this connection, further study of the properties of metal sulfides, both individual sulfides and sulfides modified by means of certain functional additives, in order to create catalysts with an increased activity in low-temperature hydrogenation processes, is becoming a task of primary importance. Another promising aspect may become the study of the catalytic properties of various metal complexes. One may hope that, by varying the type of metal and the nature of the ligands, it will be possible to create an active and sulfur-resistant catalyst for the hydrogenation of thiolene 1,1-dioxides. Such studies may not only lead to the formation of more effective catalysts for the synthesis of thiolane 1,1-dioxide, but they may also help to develop the theory of catalysis and in particular its inadequately elucidated branch — the catalysis of reactions of organosulfur compounds.

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