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The vapour phase heterogeneous-catalytic hydrogenation of carbonyl compounds and carbon monoxide

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ABSTRACT. A systematic account is given of data on the mechanisms and kinetics of processes involving the vapour phase hydrogenation of carbonyl compounds and carbon monoxide to hydrocarbon on transition metals. The activity and selectivity series in relation to the reduction of the carbonyl group and CO are determined mainly by the energies of the bonds formed by the compounds hydrogenated and hydrogen with the metal. The bond energy depends in its turn both on the chemical nature of the metal and on the degree of its dispersion. The role of the geometrical factor, which influences the concentration of the active centres, is also examined.

Rules for the selection of catalysts for the hydrogenation of carbonyl compounds and CO on transition metals have been formulated on the basis of the relations discovered between the physicochemical and catalytic properties.

The bibliography includes 110 references.

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I. Introduction

Processes involving the heterogeneous-catalytic hydrogenation of carbonyl compounds (aldehydes, ketones, etc.) include a large number of reactions of practical interest, especially when it is possible to achieve them at low temperatures and atmospheric pressure. At the same time, these reactions have been little investigated and only recently has there been a greater interest in them.

Carbon monoxide may be regarded as the simplest representative of carbonyl compounds and syntheses based on it make it possible to obtain a large number of products of practical value.

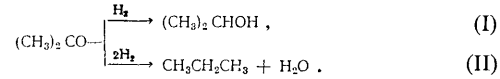
Despite the large variety of the hydrogenation reactions of carbonyl compounds, they have many features in common, whose discovery should promote the development of theoretical principles for the prediction and selection of catalysts.

The present review will consider mainly studies carried out in recent years on the mechanisms, kinetics, and catalyst selection rules for processes involving the gas-phase hydrogenation of carbonyl compounds as well as CO to hydrocarbons. The liquid-phase hydrogenation of aldehydes, ketones, and unsaturated oxo-compounds in solutions at an elevated pressure has been described in detail in other reviews and monographs.[1–4]

II. Thermodynamics of processes involving the hydrogenation of carbonyl compounds and carbon monoxide

Depending on the reaction conditions and the catalyst used, the hydrogenation of carbonyl compounds can result in the formation of alcohols, hydrocarbons, and also reduction products with retention of the carbonyl group.

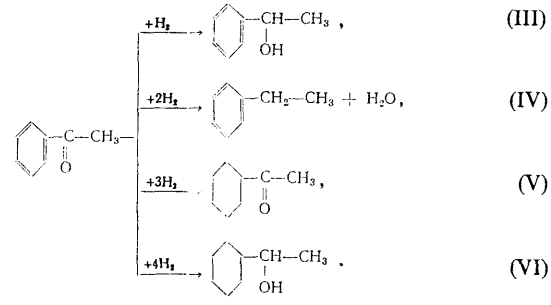
The reduction of acetone in the presence of metal catalysts takes place mainly with formation of isopropyl alcohol and propane:[5]



(I)

(II)

The interaction of acetophenone with hydrogen leads to a more complex composition of the product, because in this case there is a possibility of both the hydrogenation of the aromatic rings and of the complete or partial reduction of the carbonyl group:[5]



(III)

(IV)

(V)

(VI)

The standard Gibbs free energies ΔG_r° of the hydrogenation of acetone (in the range 300–450 K) and acetophenone (at 300–600 K) and the corresponding equilibrium constants K_e, found at a pressure

of 0.1 MPa, are listed in Table 1. Evidently in the temperature range from 300 to 600 K the equilibrium constants of reactions (II) and (IV) are several orders of magnitude higher than the K_{ei} of reactions (I) and (III). Consequently at the above temperatures the complete reduction of acetone to propane and of acetophenone to ethylbenzene is thermodynamically more favourable.

The similarity of the K_{ei} for reactions (I) and (III) and also for reactions (II) and (IV) indicates a comparatively small influence of the nature of the substituent at the carbonyl group on the thermodynamic probability of its reduction. The hydrogenation of the aromatic ring of acetophenone is easier than the reduction of the carbonyl group.

With increase in temperature (in the range 300–600 K), the equilibrium constants of the reactions involving the reduction of the carbonyl group and the hydrogenation of the aromatic ring of acetophenone diminish. Analysis of the constants K_{ei} shows that, in the experimental temperature range, reactions (II) and (IV)–(VI) are almost irreversible in contrast to reactions (I) and (III). An increase in the overall pressure of the systems to 1–10 MPa makes it possible to raise the equilibrium yield of isopropyl alcohol and methylphenylmethanol to 75–100 mol %.[5]

A thermodynamic analysis of the principal acetone hydrocondensation reactions involving the formation of higher (C_6-C_9) alcohols, ketones, and hydrocarbons and oxygen-containing compounds from CO and H_2 has been considered.[7,8] The temperature dependence of the equilibrium constants of the reactions involving the formation of methane and its homologues, i.e.

$$CO+3H_2=CH_4+H_2O, \qquad \text{(VII)}$$

$$n\text{CO}+(2n+1)H_2=C_nH_{2n+2}+nH_2O \quad (n\geqslant 2), \qquad \text{(VIII)}$$

from the synthesis gas is presented in Table 2.[8] Evidently, with increase in temperature, the thermodynamic probability of the synthesis of methane homologues falls. However, it remains high for all hydrocarbons (up to ~700 K). The differences between the thermodynamic probabilities of the formation of hydrocarbons of different types are unimportant, since the process selectivity is determined by kinetic and not thermodynamic factors. The available data[8] make it possible to calculate the equilibrium compositions of products with a specified number of carbon atoms in the molecule.

Table 2. Temperature dependence of the equilibrium constants of the CO + H_2 reactions.[8]

Hydrocarbon formed	$\lg K_e$			
	300 K	500 K	700 K	900 K
CH_4	24.7	10.1	3.6	—0.1
C_2H_6	37.4	12.7	1.8	—4.4
C_6H_{14}	94.9	27.4	—2.4	—12.1
$C_{10}H_{22}$	152.3	41.8	—6.9	—34.2
$C_{20}H_{42}$	295.6	77.8	—18.0	—71.9
cyclo-C_6H_{12}	89.5	24.9	—3.6	—19.7
cyclo-$C_6H_{11}-CH_3$	106.1	30.0	—3.5	—22.3

III. Characteristics of the adsorption of reactants on the surfaces of metal catalysts

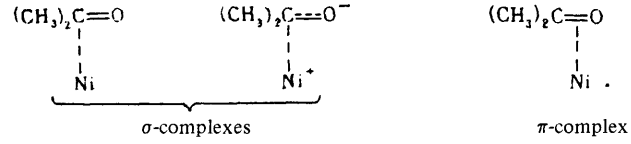
1. Adsorption of carbonyl compounds

The structure and nature of the surface species formed in the adsorption of carbonyl compounds on metal catalysts have been investigated mainly by IR spectroscopy. It has been found[9] that at 298 K acetone on the iron surface forms the π-complex $(CH_3)_2C{=}O$ (O → Fe). At the same time, the spectrum contains absorption bands characterising the alkoxy-groups $(CH_3)_2CO-Fe$. On nickel and cobalt, extensive decomposition of the acetone molecule to carbon monoxide has been observed. The presence in the IR spectra of

Table 1. Temperature dependence of the standard Gibbs free energies (in kJ mol^{-1}) and equilibrium constants (in kPa^{-1}) in reactions (I)–(VI).[5]

T, K	Reactions											
	(I)		(II)		(III)		(IV)		(V)		(VI)	
	$-\Delta G_r^0$	K_e	$-\Delta G_r^0$	K_e	$-\Delta G_r^0$	K_e	$-\Delta G_r^0$	K_e	$-\Delta G_r^0$	K_e	$-\Delta G_r^0$	K_e
300	20.31	$3.55\cdot10^5$	98.82	$1.778\cdot10^{19}$	20.31	$3.55\cdot10^5$	99.53	$1.995\cdot10^{19}$	151.4	$3.162\cdot10^{28}$	169.58	$3.981\cdot10^{31}$
325	17.97	$9.1\cdot10^4$	96.14	$3.2\cdot10^{17}$	—	—	—	—	—	—	—	—
350	14.63	$1.5\cdot10^4$	93.26	$8\cdot10^{15}$	14.13	$1.3\cdot10^4$	94.01	$1.21\cdot10^{16}$	163.15	$2.512\cdot10^{26}$	174.43	$1.120\cdot10^{28}$
375	10.87	$3.3\cdot10^3$	88.62	$4\cdot10^{14}$	—	—	—	—	—	—	—	—
400	8.57	$1.3\cdot10^3$	87.78	$4\cdot10^{13}$	7.98	$1.1\cdot10^3$	89.54	$5\cdot10^{13}$	174.43	$6.31\cdot10^{24}$	179.32	$2.512\cdot10^{25}$
425	3.34	$3.0\cdot10^2$	81.76	$3\cdot10^{12}$	—	—	—	—	—	—	—	—
450	—	—	80.34	$4\cdot10^{11}$	1.80	$1.6\cdot10^2$	81.97	$3\cdot10^{11}$	180.5	$5.01\cdot10^{23}$	184.17	$2.51\cdot10^{22}$
500	—	—	—	—	—4.35	40	77.54	$0.13\cdot10^{10}$	198.3	$5.01\cdot10^{23}$	189.06	$5.6\cdot10^{21}$
550	—	—	—	—	—	—	70.39	$0.5\cdot10^9$	210.05	$7.9\cdot10^{21}$	193.91	$3\cdot10^{20}$
600	—	—	—	—	—	—	59.94	$0.2\cdot10^7$	217.57	$7.9\cdot10^{20}$	194.62	$9\cdot10^{18}$

absorption bands in the range 1570–1700 cm^{-1} indicates the presence of π-complexes on the nickel and cobalt surfaces. In a study of the adsorption of acetone and of its deuteriated derivatives on Ni/SiO_2 in the temperature range 298–473 K, Young and Sheppard[10] suggested the possibility of forming two types of complexes between nickel and the ketone:



The adsorption of acetone on the 5% Ru/Al_2O_3 catalysts, differing in the content of preadsorbed hydrogen, has been investigated by IR spectroscopy. The authors[11] believe that, regardless of the presence or absence of H_2 on the ruthenium surface, acetone is hydrogenated on platinum group metals[12] via the formation of only alkoxy-groups and that π-complexes are not produced.

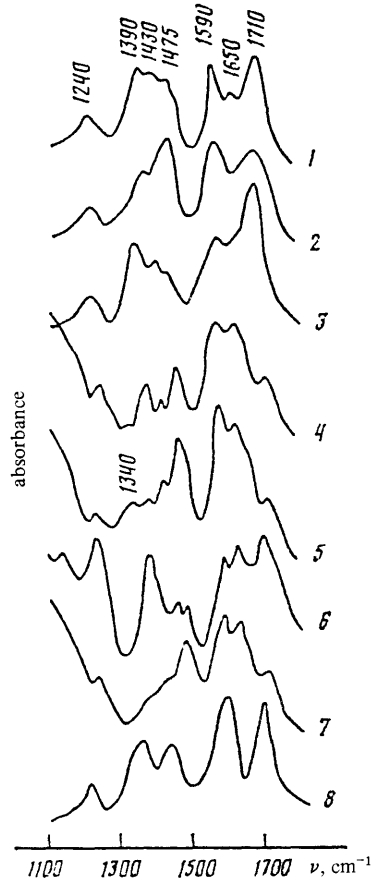


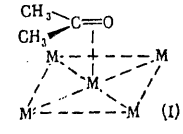
Figure 1. IR spectra of acetone adsorbed on deposited metals: *1*, Fe; *2*, Co; *3*, Ni; *4*, Ru; *5*, Rh; *6* Ir; *7*, Pt; *8*, Cu.

The IR spectra of acetone adsorbed on deposited transition metals, obtained under conditions close to those in the catalytic reaction (I), are presented in Fig. 1.[13–15] Acetone is hardly adsorbed on the surface of the Pd/Al_2O_3 catalyst—the corresponding absorption band could not be detected in the IR spectrum. The observed shift ($\Delta\nu \simeq 20$ cm^{-1}) of the maximum of the band corresponding to the vibration of the carbonyl group [$\nu(CO) = 1740$ cm^{-1}] has been explained by the presence of a weak chemisorption bond between the CO groups of acetone and the OH groups on the γ-Al_2O_3 surface, which corresponds to the formation of complexes with the $(CH_3)_2C=O...H-O-Al\langle^{O-}_{O-}$ hydrogen bond.[16] A new absorption band in the range 1590–1605 cm^{-1} appears in the spectrum of acetone adsorbed on metal catalysts. In addition, an absorption band in the range 1640–1650 cm^{-1} has been detected after adsorption on Fe, Ru, Rh, Ir, and Pt. When $(CH_3)_2CO$ is adsorbed on deposited transition metals (M), there is a possibility of the formation of a donor–acceptor complex when π-electrons are transferred from the ketone molecule to the unoccupied *d* orbitals of the metal or a dative interaction may take place, in which the *d* electrons of the metal are localised in the antibonding π* orbitals of the carbonyl group.[17]

The direction of the shift of the electron density in the adsorption complex depends on the ratio of the electronegativities of the metal atom and the ketone molecule. The electronegativity of the $(CH_3)_2CO$ molecule is determined by the electronegativities of the carbon and oxygen atoms of the carbonyl groups, which are respectively 2.55 and 3.44 on the Pauling scale.[18] The electronegativities of metals on this scale decrease in the sequence

$$Pt(2.28),\ Ru(2.28) > Ir(2.2),\ Rh(2.2) > Ni(1.91) > Cu(1.90) > Co(1.88) > Fe(1.8). \qquad (IX)$$

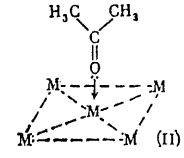
Taking into account the greater electronegativity of the acetone molecule compared with that of the metal atoms, it has been suggested[13–15] that in the system considered the dative interaction predominates over the donor–acceptor interaction, so that the appearance of the absorption band in the range 1590–1605 cm^{-1} characterises the formation of a planarly oriented π-complex (I) on the surfaces of the catalysts investigated:



(I).

The energy of the dative interaction increases with decrease in the electronegativity of metals, so that acetone should be adsorbed most strongly on the catalyst located at the end of the series (IX), which agrees with experimental data.[13]

In conformity with the work of Blyholder and co-workers,[9,19] the absorption band in the range 1640–1650 cm^{-1} has been assigned[13,15] to the formation of a donor–acceptor complex:



(II)

in which the molecular orbital of the CO group overlaps the unoccupied *d* orbital of the metal.

The conclusions concerning the structure of the adsorption complexes were confirmed by our quantum-chemical calculations on the interaction of acetone with Ni and Cu clusters, carried out by

the INDO method.[20] It follows from the results that the formation of a "parallel" π-complex (I) with an acetone molecule is more likely for the Cu cluster, whereas for the Ni cluster the probabilities of the formation of the complexes (I) and (II) are approximately the same. Regardless of the nature of the metal (Ni, Cu), the loosening of the C=O bond in the π-complex (I) is greater than in the donor–acceptor complex (II). This permits the conclusion that the π-complex (I) is the most probable intermediate in the catalytic hydrogenation of acetone.

Acetone and other carbonyl compounds form type (II) complexes with the surface of simple and mixed oxides used as carriers for metal catalysts, while hydrogen-bonded complexes are produced on coordination to surface OH groups.[16,39,40] The adsorption of acetone on the surfaces of oxides may be accompanied by aldol and crotonic condensations, whose mechanisms (for γ-Al_2O_3) were investigated in our previous studies.[16,41]

2. The adsorption of carbon monoxide

The experimental and calculated data for the adsorption of CO on transition metals has been described systematically in monographs[21–24] and reviews.[25–28] Depending on the nature of the metal and the adsorption conditions, the CO molecule initially forms a weak one-electron bond, which is rapidly converted into stronger bonds: a linear bond with one metal atom and a bridge bond with two or more M atoms:[26]

$$M + CO \rightleftarrows M^- \ldots CO^+ \rightleftarrows M{-}C{\equiv}O \overset{M}{\rightleftarrows} \begin{matrix} M \\ M \end{matrix}\!\!>\!C{=}O. \qquad (X)$$

Quantum-chemical calculations[29] on the interaction of CO with iron, cobalt, nickel, and copper atoms with formation of the linear form of the M–CO bond have shown that the M–C bond strength diminishes in the sequence Fe > Co, Ni > Cu, whilst the energy of the M–O bond increases in the sequence Ni < Co < Cu < Fe. The calculated data agree well with the IR spectroscopic results,[30,31] on the basis of which it has been concluded that there is a dative bond between the above metals and the CO molecule involving the formation of the π-complex (the alkoxy-complex is hardly formed). The following sequence based on decreasing M–C bond strengths has been established for platinum group metals on the basis of absorption spectra:[32–34]

$$Ir > Ru > Pt > Rh > Pd.$$

According to quantum-chemical calculations,[35] the average M–CO bond energy diminishes with increase in electronegativity in series (IX), while the strength of the C–O bond in the adsorbed molecule increases, so that the presence of metals with the lowest electronegativity (Fe, Co) should promote to the greatest extent the rupture of the CO bond and the formation of hydrocarbons via the reaction between CO and H_2. This conclusion has been confirmed by numerous experimental data.[36–38]

The adsorption of CO on simple and mixed oxides of non-transition metals results in the formation of carboxylate and carbonate structures of different types.[22,24]

3. The adsorption of hydrogen

The adsorption properties of massive and dispersed metal catalysts in relation to hydrogen have been investigated in fair detail.[2,22,23,25,42] Analysis of the available and experimental calculated data shows that the dissociative form of the adsorption of H_2 predominates on Group VIII metals; on copper, hydrogen is adsorbed in the form of molecules,[43] whilst on ruthenium both molecular[15] and dissociative[23] forms of adsorption of H_2 are observed (depending on the adsorption conditions and the degree of dispersion of the metal).

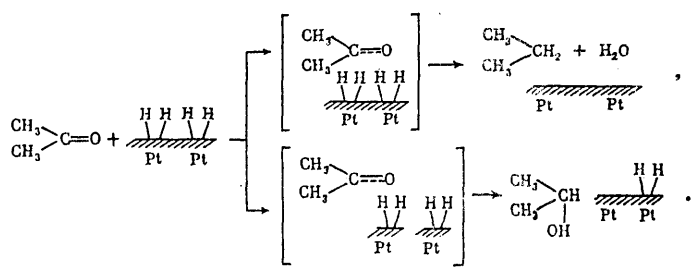
IV. The mechanism and kinetics of the hydrogenation of ketones and CO

1. Hydrogenation of acetone

When reaction (I) was carried out on sputtered metal films, it was shown[44] that the rate of the process r is independent of the partial pressure of acetone P_A, depends in a complex manner on the partial pressure of hydrogen P_{H_2}, and is inhibited as the concentration of the reaction product (isopropyl alcohol) increases. The kinetic equation $r = kP_A^{1.2}P_{H_2}^{1.5}$, where k is the reaction rate constant, has been proposed[45] for the reaction on Raney nickel.

The kinetic orders of reaction (I) have been determined[46,47] and a kinetic equation, describing the process on an inhomogeneous surface in the region of reversibility, has been devised in addition.[47] It has been suggested[44,47] that the rate of the reaction is determined by the stage involving the surface interaction of the adsorbed acetone molecules with the hydrogen atoms or molecules.

The following parallel mechanism of the hydrogenation of acetone to propane and alcohol on a diatomic active centre of the catalyst has been proposed[48] in the case of platinum black:



The kinetics of the vapour-phase hydrogenation of acetone on massive nickel, cobalt, copper, and their alloys have been studied in detail by Avetisov and Gel'bshtein and co-workers.[49–52] It has been shown[49] that the rate of reaction increases appreciably with increase in P_A, depends to a lesser extent on P_{H_2}, and is inhibited by the isopropyl alcohol formed. The observed reaction orders with respect to the components are variable and depend on their concentrations and temperature. It has been suggested[49] that hydrogen atoms adsorbed on nickel in the H^+-form enter into the reaction and that the rate of this process is limited by the surface interaction of the adsorbed ketone molecules and H atoms. It has been assumed[49] that acetone and hydrogen are adsorbed on different active centres of the catalyst surface. The non-planar acetone molecules do not then occupy all the adsorption centres on the metal surface even when the latter is fully saturated. On these grounds, it has been postulated[49] that hydrogen atoms are adsorbed on the metal surface in the gaps between the ketone molecules. An adsorption mechanism of reaction (I) has been put forward on the basis of kinetic data and the corresponding equation, which describes satisfactorily the experimental relations, has been derived.[49]

The kinetic relations and the reaction mechanism characteristic of the reactions on nickel are retained on the cobalt catalyst and nickel–cobalt alloys containing between zero and approximately 50 at.% of cobalt.[52]

It has been established[50] that, in the presence of massive copper, the rate of reaction hardly depends on P_A, increases with increasing P_{H_2}, and diminishes with increasing partial pressure of isopropyl alcohol P_{al}. On the basis of the results of studies[53,54] in which it had been shown that at temperatures below 573 K hydrogen is not adsorbed on copper, Babkova et al.[50] examined different versions of the impact (with respect to H_2) mechanism of the hydrogenation of acetone.

The hypothesis[50] that the hydrogenation of acetone on copper can be described with the aid of the mechanism proposed by Twigg[55] for the hydrogenation of ethylene on nickel as applied by Temkin[56] to the hydrogenation of ethylene on a palladium membrane is interesting. This mechanism can be represented schematically as follows:

Scheme 1

1) $(CH_3)_2CO + Z \rightleftarrows Z(CH_3)_2CO$,
2) $Z(CH_3)_2CO + Z_1 + H_2 \rightleftarrows Z(CH_3)_2COH + Z_1H$,
3) $Z(CH_3)_2COH + Z_1H \rightarrow Z(CH_3)_2CHOH + Z_1$,
4) $Z(CH_3)_2CHOH \rightleftarrows (CH_3)_2CHOH + Z$,

where Z and Z_1 are adsorption centres on the catalyst surface.

Hydrogen from the gas phase interacts with an adsorbed acetone molecule (on the adsorption centre Z), which results in the formation of a partly hydrogenated form of acetone and a hydrogen atom adsorbed on a free centre (Z_1) on the copper surface. The ability of copper to adsorb atomic hydrogen has been reliably established.[57] On the basis of the scheme described above, equations describing the experimental data in the experimental temperature and reactant concentration ranges have been proposed.[50]

The similarity of the kinetics of the acetone hydrogenation reaction catalysed by nickel and nickel–copper alloys with a copper content up to 60 at.% suggested[51] that the mechanism proposed[50] for the hydrogenation of acetone on the nickel catalyst is valid also for the nickel–copper alloy having the composition indicated above. For a higher copper content in the alloy (> 60 at.%), acetone is hydrogenated in conformity with Twigg's mechanism describing the reaction on the copper catalyst.

The kinetics of the reversible hydrogenation of acetone on the nickel catalyst have been investigated.[47,58] The hydrogenation reaction proceeds via two pathways: the adsorbed ketone molecule reacts with adsorbed hydrogen atoms and a partly hydrogenated acetone molecule reacts either with gas-phase hydrogen or with a second adsorbed hydrogen atom. The dehydrogenation of isopropyl alcohol includes a stage in which the gas-phase alcohol interacts with the dissociatively adsorbed hydrogen.[47,58]

The kinetics of the hydrogenation of acetone in a differential flow reactor at 423 K in the presence of Cu, Pt, Pd, and Rh deposited on kieselguhr have been studied.[59] 29 kinetic equations, corresponding to the Langmuir–Hinshelwood mechanism, have been analysed by the ECV method. The activity of the platinum group metal diminishes in the following sequence according to the reaction rate constants (k expressed in mol/h kg of catalyst): Pt > Rh > Pd. The activities of the catalysts investigated lie in the following sequence in terms of the initial rate of hydrogenation: Cu > Rh > Pt > Pd. The series presented must be regarded as arbitrary, since the concentrations of the metals deposited on kieselguhr were different and the specific surfaces of the metals were therefore also different. Furthermore, at temperatures above 737 K it is essential to take into account the reversibility of the acetone hydrogenation reaction,[5] which was not done in the above study.[59]

The experimental relations obtained in the presence of the copper catalyst were described[59] by a kinetic model according to which the molecularly adsorbed hydrogen reacts with a dissociatively adsorbed acetone molecule, but the authors do not explain what they mean by the dissociative adsorption of acetone on copper and what is the mechanism of this process. The kinetic equations proposed[59] for the description of the processes occurring on platinum group metals (Pt, Rh, Pd) are consistent with the mechanism according to which the rate is determined by the interaction between the adsorbed hydrogen and acetone molecules. However, these conclusions conflict with numerous literature data, according to which the atomic form of the adsorption of hydrogen predominates on the surface of platinum metals.

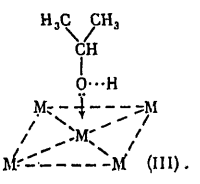
We carried out a systematic study of the vapour-phase hydrogenation of acetone on deposited and massive transition metals.[13–15,60–65] Detailed investigation of the kinetics of reaction (I) at different temperatures showed that the following picture is observed in all cases: the rate of the process increases with increasing concentrations of the reactants, reaching saturation. The reaction product (isopropyl alcohol) does not inhibit the hydrogenation of acetone on all catalysts other than the copper and ruthenium catalysts, where a decrease in rate with increase in P_{Al} was observed.[14,15]

The study of the mechanism and kinetics of the reverse reaction—the dehydrogenation of isopropyl alcohol on the Pt/Al_2O_3 catalyst, i.e.

$$(CH_3)_2CHOH \rightarrow (CH_3)_2CO + H_2, \qquad (XI)$$

demonstrated the following features: with increase in P_{Al} and for low values of P_{H_2}, the rate of reaction (XI) increases, reaching saturation. In the presence of an excess of hydrogen, the order of the reaction with respect to the alcohol increases, approaching unity. The reaction products (acetone and hydrogen) then inhibit reaction (XI).

These results made it possible, in the first place, to account for the influence of the alcohol concentration on the kinetics of reaction (I). The character of this influence depends significantly on the degree of coverage of the metal surface by hydrogen θ_H, which affects the adsorption of isopropyl alcohol on the metal surface. The isopropyl alcohol molecule, which has no unsaturated bonds, is adsorbed (perpendicularly) on the metal surface as a result of the dissociation of the OH group. This leads to the formation of the alkoxy-structure[64]



(III).

In the joint adsorption of $(CH_3)_2CHOH$ and H_2 molecules, competition is observed:[64] the atomically adsorbed hydrogen prevents the dissociation of the OH group of the isopropyl alcohol molecule and the adsorption of the latter on the metal. This is manifested clearly in the dehydrogenation of isopropyl alcohol, where an increase in P_{H_2} in the reaction mixture leads to the inhibition of reaction (XI) and an increase in the reaction order with respect to the alcohol.

The following mechanism for the reversible addition of hydrogen to the carbonyl group has been proposed[64,65] on the basis of the entire set of adsorption and kinetic data obtained:

Scheme 2

1) $H_2 + 2Z_H = 2Z_HH$,
2) $(CH_3)_2CO + Z_A = Z_A(CH_3)_2CO$,
3) $Z_A(CH_3)_2CO + Z_HH \rightleftarrows Z_A(CH_3)_2COH + Z_H$,
4) $Z_A(CH_3)_2COH + Z_HH \rightleftarrows Z_H(CH_3)_2CHOH + Z_A$,
5) $Z_H(CH_3)_2CHOH = (CH_3)_2CHOH + Z_H$,

where Z_A and Z_H are the centres for the adsorption of acetone and hydrogen respectively.

The equilibrium adsorption of the initial reactants takes place in the first two stages: acetone forms the π-complex (I) on the polyatomic centre Z_A, while the dissociative adsorption of hydrogen takes place on single M-centres Z_H.

Our data make it possible to justify and specify in detail the physical significance of the active centres (Z_A and Z_H) postulated by Babkova et al.[49]

The study of the IR spectra of the acetone adsorbed on metals[13–15] (Fig. 1) led to the conclusion that at the temperatures of the catalytic reaction (~330–370 K) the ketone molecule is oriented "parallel" to the metal plane [the complex (I)]. For this orientation, acetone is adsorbed only on specific groups of M atoms with a suitable geometry (of the type of Balandin's multiplets). The fraction λ of such complex centres Z_A is small, so that acetone hardly affects the adsorption of H_2 on single centres Z_H (on the rest of the surface), whose fraction is close to unity. Since the transition state (the rate-limiting stage of the process) is formed on a pair of centres $Z_A + Z_H$, the number of active centres (n_a) for the catalytic reaction should be small. The quantity n_a enters into the expression for the pre-exponential factor k_L^0 in the expression for the rate constant for the rate-limiting stage:[66]

$$k_L^0 = \kappa(k_BT/h)n_a \exp(\Delta S_L^*/R),$$

where k_BT/h is the frequency factor, κ the transmission coefficient, usually equal to unity, ΔS^*_L the entropy of activation, and R the gas constant. Since ΔS^*_L for stages of the type $A_{ads} + B_{ads} = C_{ads}$ is usually small in absolute magnitude,[67] we have $k_L^0 \simeq (k_BT/h)_a$, so that an increase in k_L^0 with decrease in the degree of dispersion of the metal, up to a certain limit corresponding to the $(n_a)_{max}$, is to be expected. This corresponds to a situation such that the probability of the existence of the complex groups Z_A on the planes of the microcrystals increases as the metal particles grow (with This corresponds to a situation such that the probability of the existence of the complex groups Z_A on the planes of the micro-crystals increases as the metal particles grow (with increase in $\bar{d}$) and the fraction of the active surface also increases, reaching saturation, whereupon the fraction of the planar M atoms becomes virtually unity. Fig. 2 confirms this, catalysts of different chemical composition, characterised by different activation energies E_L, fitting on a single straight line. Comparison of the experimental maximum values of $k_L^0 \simeq 10^6$ (Table 3) with the "normal" value $k_L^0 = 10^7$–10^8 mol m^{-2} × s^{-1}, corresponding to $\gamma = 1$, shows that the fraction of the working surface λ is only a few per cent even on large crystals.

The ideas described are also confirmed by the results of a study[68] in which it has been established that the adsorption of acetone and hydrogen in the presence of the Pt/Al_2O_3 catalyst with different degrees of dispersion takes place without competition. The activity of the catalyst increases with increase in the size of the Pt system from 5 to 20 nm and then remains constant.

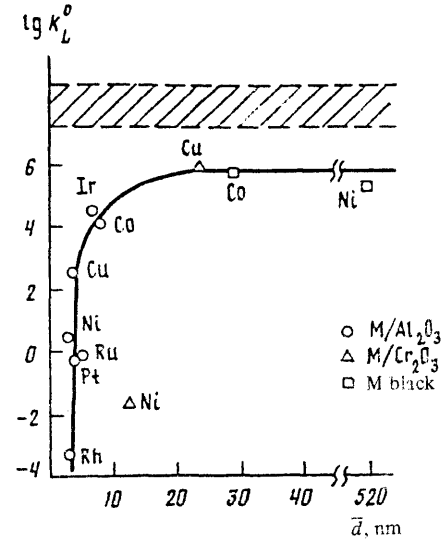


Figure 2. Dependence of the pre-exponential factor of the rate constant for the rate-limiting stage on the hydrogenation of acetone on the degree of dispersion of the metal. The dashed lines represent the values of k_L^0 corresponding to the entire working surface ($\lambda = 1$) for $\Delta S_L^* \simeq 0$–20 J mol^{-1} K^{-1}.

Table 3. Kinetic and thermodynamic characteristics of the acetone hydrogenation reaction on metals.

Catalyst	$\bar{d}$ for metal, nm	$10^7 r^*$, mol m^{-2} s^{-1}	E_L, kJ mol^{-1}	$10^7 k_L^{**}$, mol m^{-2} s^{-1}	k_L^0, mol m^{-2} s^{-1}	$10^{-5} b_A^{**}$, Pa^{-1}	q_A, kJ mol^{-1}	ΔS_A^*, J mol^{-1} K^{-1}	q_C, kJ mol^{-1}
Pt/Al_2O_3	3.9	44	31	65.4	0.38	7	12.5	—21	—
Ir/Al_2O_3	6.8	11.7	71	2.5	$3 \cdot 10^4$	73.5	83	—191	—
Rh/Al_2O_3	2.5	7.7	17	16	$6 \cdot 10^{-4}$	12	14	—22	—
Ni/Al_2O_3	2.4	7.5	43	6.6	3.0	58.5	83	—214	—
Ru/Al_2O_3	4.4	7.0	39	20	0.8	35	34	—72	40
Cu/Al_2O_3	3.0	5.0	58	3.3	$3 \cdot 10^2$	120	80	—197	86
Co/Al_2O_3	7.5	4.6	68	2.5	$9 \cdot 10^3$	150	81	—197	—
Pd/Al_2O_3	5.0	inactive							
Fe/Al_2O_3	4.2	»							
Cu/Cr_2O_3	23	30	70	132	$9.8 \cdot 10^5$	80	39	—77	92
Ni/Cr_2O_3	11.5	15.3	26	21	$2.1 \cdot 10^{-2}$	10	24	—53	—
Ni black	520	15.8	72	16.6	$2.5 \cdot 10^5$	12	32	—83	—
Co black	28.4	3.0	80	2.2	$5.8 \cdot 10^5$	15	42	—112	—
Cu black	1170	inactive							
Au ***		$2 \cdot 10^{-4}$							

Note. Mixture composition; $P_A = 10$, kPa, $P_{H_2} = 50$ kPa.

*Calculated for 364 K.

**Calculated for 337 K.

***The data of Stoddart and Kemball[44] are quoted.

It follows from the competing adsorption of hydrogen and isopropyl alcohol that these substances are bound to the same centres (Z_H) and that the alcohol forms the complex (III). The equilibrium desorption of the product takes place in stage 5. Stages 3 and 4 are reversible but non-equilibrium. At low temperatures stage 3 is slowest.[64]

The observed rate of reaction of acetone under stationary conditions is

$$r = r_3 - r_{-3} = r_4 - r_{-4}, \quad (1)$$

where $\gamma \pm i$ are the rates of the stages in the forward and reverse directions. When account is taken of Eqn. (1), the overall kinetic equation for the reversible hydrogenation of acetone, corresponding to Scheme 2, is

$$r = r_3 - r_{-3} = k_3 \frac{b_A P_A}{1 + b_A P_A + l} \frac{\sqrt{b_{H_2} P_{H_2}}}{1 + \sqrt{b_{H_2} P_{H_2}} + b_a P_a} - k_{-3} \frac{l}{1 + b_A P_A + l} \frac{1}{1 + \sqrt{b_{H_2} P_{H_2}} + b_a P_a}, \quad (2)$$

in which $k_{\pm i}$ are the rate constants for the stages in the forward and reverse directions and b_A, b_{H_2}, and b_a are the adsorption coefficients of acetone, hydrogen, and the alcohol respectively, and

$$l = (k_3 b_A P_A + k_{-4} b_a P_a)/(k_4 \sqrt{b_{H_2} P_{H_2}} + k_{-3}).$$

The quantity l represents the "degree of reversibility of the reaction"[64,65] and is equal to the fraction of the centres Z_A occupied by the same hydrogenated form of acetone. Eqn. (2) agrees quantitatively with experimental data for the kinetics of reaction (I) in both the forward and reverse directions: the inhibiting effect of hydrogen on the adsorption of the alcohol is then clearly manifested.[64]

Under conditions remote from equilibrium (at low temperatures where $l \to 0$), acetone is hydrogenated by the mechanism presented in Scheme 3:

Scheme 3

1) $H_2 + 2Z_H = 2Z_H H$,
2) $(CH_3)_2CO + Z_A = Z_A(CH_3)_2CO$,
3) $Z_A(CH_3)_2CO + Z_H H \rightarrow Z_A(CH_3)_2COH + Z_H$,
4) $Z_A(CH_3)_2COH + Z_H H \xrightarrow{fast} Z_H(CH_3)_2CHOH + Z_A$,
5) $Z_H(CH_3)_2CHOH \xrightarrow{fast} (CH_3)_2CHOH + Z_H$.

In this case Eqn. (2) assumes a simpler form[13,15] (the term characterising the reverse reaction is missing) and describes satisfactorily the kinetic data for the forward process in the presence of all the catalysts investigated (Table 3) with the exception of copper and ruthenium. When the copper and ruthenium catalysts are used, account must be taken of the observed inhibition of reaction (I) by the isopropyl alcohol formed and of the involvement in the reaction of the hydrogen adsorbed in the molecular form, which we have established by the programmed thermal desorption method.[15,43] Scheme 3 must therefore be modified somewhat:

Scheme 4

1) $H_2 + Z_H = Z_H H_2$,
2) $(CH_3)_2CO + Z_A = Z_A(CH_3)_2CO$,
3) $Z_A(CH_3)_2CO + Z_H H_2 \rightleftarrows Z_H(CH_3)_2CHOH$,
4) $Z_H(CH_3)_2CHOH = (CH_3)_2CHOH + Z_H$.

Here too the rate-limiting stage is the interaction of the adsorbed starting materials, while in the remaining stages equilibrium is established. The kinetic equation

$$r = k_3 \frac{b_A P_A}{1 + b_A P_A} \frac{b_{H_2} P_{H_2}}{1 + b_{H_2} P_{H_2} + b_a P_a},$$

which describes satisfactorily the experimental data for the Cu and Ru catalysts,[14,15] corresponds to this mechanism (Scheme 4).

The study of the individual stages of the mechanism of the hydrogenation of acetone on transition metals has shown[65] that, if the reactive π-complex (I) is formed on adsorption of the ketone, then partial reduction of the complex leads only to isopropyl alcohol. When acetone is adsorbed as the donor–acceptor complex (II), the carbonyl group of the ketone is fully reduced with elimination of the oxygen atom. Bearing in mind that acetone and other ketones are weak Lewis bases, we achieve such alteration in the form of adsorption and in the mode of reaction[69] by using bifunctional catalysts containing, apart from the transition metals, also strong Lewis acid centres L to which the oxygen of the carbonyl group is bound via the unshared electron pair. Hydrogen is activated on the metal. We propose[70] the following two pathway mechanism (Scheme 5) of the complete reduction of the carbonyl group of acetone [reaction (II)]:

Scheme 5

1) $H_2 + 2Z_H = 2Z_H H$,
2) $(CH_3)_2CO + Z_L = Z_L(CH_3)_2CO$,
3) $Z_L(CH_3)_2CO + Z_H H = Z_L(CH_3)_2COH + Z_H$,
4) $Z_L(CH_3)_2COH + Z_H H = Z_L(CH_3)_2CHOH + Z_H$,
5) $Z_L(CH_3)_2CHOH = (CH_3)_2CHOH + Z_L$,
6) $Z_L(CH_3)_2COH + Z_H H \rightarrow Z_L C_3H_6 + H_2O + Z_H$,
7) $Z_L C_3H_6 + Z_H H \rightarrow Z_L C_3H_7 \xrightarrow{Z_H H} C_3H_8 + Z_L + 2Z_H$.

Equilibrium is established in stages 1–5 which determine the rate of formation of isopropyl alcohol. Stage 3 is common to the synthesis of the alcohol and the hydrocarbon. The rate of the total hydrogenation of acetone is limited by Stage 6, in which the addition of a H atom to the adsorbed semihydrogenated form of the acetone is accompanied by dehydration and the formation of adsorbed propene $Z_L C_3H_6$ in the form of a π-allyl complex,[71] which is then rapidly hydrogenated to propane in a single stage.

The following kinetic equation corresponds to Scheme 5:

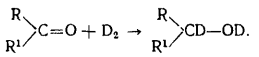
$$r = k_6 \frac{K_3 b_A P_A \sqrt{b_{H_2} P_{H_2}}}{1 + b_A P_A \left(1 + K_3 \sqrt{b_{H_2} P_{H_2}}\right) b_a P_a} \frac{\sqrt{b_{H_2} P_{H_2}}}{1 + \sqrt{b_{H_2} P_{H_2}}}, \quad (3)$$

where k_6 is the rate constant for the rate-limiting stage and K_3 the equilibrium constant for the third stage. Eqn. (3) describes satisfactorily[70] the experimental and kinetic data for the complete hydrogenation of acetone in the presence of the bifunctional catalyst.

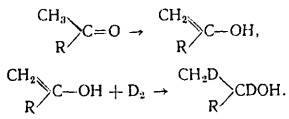
As a result, the kinetic and thermodynamic characteristics of the different stages in the mechanisms of the acetone hydrogenation reactions occurring via Schemes 2–5 were calculated from experimental data for the catalysts listed in Table 3: the rate constants, the adsorption coefficients, the activation energies, the heats (q_i) and entropies (ΔS_i^0) of adsorption, and the pre-exponential factors of the rate constants. Analysis of the data obtained yielded new arguments in support of the proposed mechanisms and made it possible to find relations between the physicochemical and catalytic properties of the substances which can be used in the selection and improvement of catalysts for the hydrogenation of carbonyl compounds. These relations will be examined below.

The mechanism of the hydrogenation of acetone and other ketones has been investigated with the aid of deuterium–hydrogen

exchange.[2,72–74] In order to describe the interaction of deuterium with carbonyl compounds, two limiting mechanisms are usually employed:[2,72] the "ketone" and "enol" mechanisms. According to the ketone mechanism, deuterium adds directly to the carbonyl group:



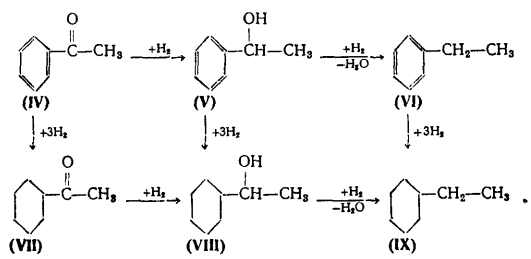
The "enol" mechanism presupposes the preliminary enolisation of the ketone and the subsequent addition of deuterium to the C=C bond:



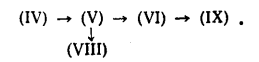
According to data[73,74] obtained in the study of the interaction of deuterium with alicyclic ketones in the presence of a prefused iron catalyst (in the temperature range from 323 to 483 K), the relative contributions of the "ketone" and "enol" mechanisms are in the proportions 1 : 1.5.

2. Hydrogenation of acetophenone

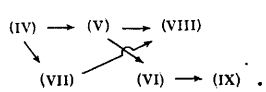
The hydrogenation of acetophenone is a complex process whose detailed mechanism has not been investigated:



Schemes for the conversion of acetophenone in the presence of nickel, platinum, and palladium have been proposed by Balandin and co-workers[75] on the basis of calculations of the adsorption energies of the index groups. On nickel, the hydrogenation process takes place in accordance with the following scheme:



For the palladium catalyst, the scheme remains the same but, as a consequence of the greater difference between the adsorption energies of the CO group and the aromatic rings, the addition of hydrogen to the ring on palladium is fairly difficult. On platinum as well as on nickel and palladium, the keto-group is most readily hydrogenated. At the same time, the reactivity of the aromatic rings in the presence of the platinum catalyst becomes higher than that of the alcoholic group, which was not observed[75] on nickel and palladium. It has therefore been suggested[75] that the hydrogenation of acetophenone proceeds according to the scheme



In terms of activity in the acetophenone hydrogenation reaction, the metals considered can be arranged in the following sequence: Ni > Pd > Pt. The hydrogenolysis on the metals indicated should proceed with much difficulty.[75]

In the hydrogenation of acetophenone on industrial catalysts (Cu–Cr–Ba; Ni–Ti–Al), it has been shown[76] that the copper–chromium–barium specimen is more selective in relation to the formation of methylphenylmethanol, while the nickel–titanium–aluminium specimen is more active in relation to the overall conversion of acetophenone. In the presence of the catalysts indicated, the process proceeds via the consecutive scheme (IV) → (V) → (VI). An empirical kinetic equation has been obtained and a mathematical model has been proposed for the process.[76]

3. Hydrogenation of aliphatic and cyclic ketones

The kinetics of the hydrogenation of aliphatic and alicyclic ketones in the presence of a premelted iron catalyst are described by the power equation[77]

$$r = kP_{\text{k}}P_{\text{H}_2}^{0.5}. \qquad (4)$$

The following mechanism, presupposing the adsorption of the reactants on the same centres (Z) of the iron catalyst, has been put forward on the basis of kinetic data for the hydrogenation of 2-octanone:[78]

Scheme 6

1) $H_2 + 2Z = 2ZH$,
2) $R^1COR^2 + Z = ZR^1COR^2$
3) $ZR^1COR^2 + ZH \rightarrow ZR^1C(OH)R^2$,
4) $ZR^1C(OH)R^2 + ZH = ZR^1CH(OH)R^2$,
5) $ZR^1CH(OH)R^2 = R^1CH(OH)R^2 + Z$.

The rate of the process is limited by the addition of the first hydrogen atom to the adsorbed ketone molecule; equilibrium is established in the remaining stages. Eqn. (4) has been used[77] to optimise the hydrogenation of alicyclic ketones (C_5, C_6) formed in the synthesis of alcohols by the oxidation of higher paraffins.

In order to optimise the phenol hydrogenation process in the manufacture of caprolactam, the kinetics of the addition of hydrogen to phenol and cyclohexanone molecules have been studied.[79] The following mechanism has been proposed for the reversible hydrogenation of cyclohexanone to cyclohexanol on nickel catalysts on the basis of kinetic measurements:[80]

Scheme 7

1) $H_2 + 2Z_H = 2Z_HH$,
2) $C_6H_{10}O + Z_c = Z_cC_6H_{10}O$,
3) $Z_cC_6H_{10}O + 2Z_HH \rightleftarrows Z_cC_6H_{11}OH + 2Z_H$,
4) $Z_cC_6H_{11}OH = C_6H_{11}OH + Z_c$,

where Z_c and Z_H are the centres for the adsorption of the ketone and hydrogen respectively. It is assumed that the two hydrogen atoms add simultaneously to the adsorbed ketone molecule. Cyclohexanone and hydrogen are adsorbed on different centres (Z_c and Z_H), of the catalyst, whose surface is regarded as effectively uniform. The kinetic equation proposed on the basis of this mechanism (Scheme 7) describes satisfactorily the experimental relations. These relations served as the basis of the mathematical model used to optimise the synthesis of cyclohexanol.[81]

The mechanisms of the hydrogenation of aliphatic and cyclic ketones (Schemes 6 and 7) are in general similar to the mechanism of the incomplete hydrogenation of acetone (Scheme 2), which we have established, while the kinetic equation (2), which we proposed for the description of the experimental relations obtained in the hydrogenation of acetone, is applicable also to the description of the

kinetics of the hydrogenation of 2-octanone established by Glebov et al.[78]

4. Hydrogenation of carbon monoxide

Numerous studies have been devoted to the hydrogenation of CO on metals, which leads mainly to the formation of methane and higher hydrocarbons.[36–38, 82–85] The proposed mechanisms[86–88] refer solely to the conversion of CO into methane and do not take into account the simultaneous formation of methane homologues. The mechanism of the formation of methane homologues has stages in common with the mechanism of the synthesis of methane itself and these common stages affect the rate of formation of CH_4.

The study of reactions (VII) and (VIII) on deposited metallic catalysts of different types (Table 4) enabled us to put forward[89–92] the following CO hydrogenation mechanism:

Scheme 8

1) $H_2 + 2Z = 2ZH$,
2) $CO + Z = ZCO$,
3) $ZCO + ZH = ZCOH + Z$,
4) $ZCOH + ZH \rightarrow ZX_0 + Z$,
5) $ZX_0 + ZH \rightarrow ZX_0' \xrightarrow{ZH} CH_4 + H_2O + Z$,
6) $ZX_0 + ZCO \rightarrow ZX_1 + Z$,
6') $ZX_1 + ZH \rightarrow ZX_1' \xrightarrow{ZH} C_2H_6 + H_2O + Z$,
7) $ZX_1 + ZCO \rightarrow ZX_2 + Z \ldots$,

where the adsorbed AX_0 species is the common intermediate in the formation of all the products. Its interaction with ZH affords methane (chain termination), while the reaction of ZX_0 with a carbon-containing species leads to a new adsorbed species ZX_1,, leading to the synthesis of higher hydrocarbons (chain propagation).

Table 4. Specific catalytic activities and selectivities of metal catalysts in the hydrogenation of CO.

Catalyst	$\bar{d}$ for metal, nm	$10^7 r^*$, mol m^{-2} s^{-1}	Selectivity w.r.t. methane S_{CH_4}
Ru/Al_2O_3	4.4	6.7	0.872
Rh/Al_2O_3	2.5	5.5	0.943
Co/Al_2O_3	7.5	5.04	0.940
Ni/Al_2O_3	2.4	4.7	0.957
Ni/Cr_2O_3	11.5	4.7	1.0
Pt/Al_2O_3	3.9	0.4	0.99
Ir/Al_2O_3	6.8	0.2	1.0
Pd/Al_2O_3	5.0	0.1	1.0
Fe/Al_2O_3	4.2	inactive	—
Cu/Al_2O_3	3.4	inactive	—

Note. Mixture composition: P_{CO} = 20 kPa, P_{H_2} = 50 kPa.

*Calculated for 548 K.

The first four stages in Scheme 8 determine the activity of the catalyst and the others determine its selectivity. It is assumed that adsorption equilibrium is established in stages 1–3, while the rate of the overall process is then determined by stage 4. The way in which ZCOH interacts with ZH, via the intermediate formation of the "enolic" form of formaldehyde ZCOH or via the formation of the surface carbide ZC with liberation of water, is immaterial for the process kinetics.

The question of the composition and structure of the carbon-containing species interacting with ZX_i is obscure. The IR spectra obtained under the conditions of the catalysis[84] usually manifest only the absorption bands of the adsorbed CO molecules which form complexes with the deposited metals [see Eqn. (X)]. Consequently, the surface concentrations of other carbon-containing intermediate compounds can be regarded as negligible.

The kinetic equation for the overall conversion of CO (in conformity with Scheme 8) can be written in the form

$$r = r_4 = k_4 \frac{K_3 b_{CO} P_{CO} b_{H_2} P_{H_2}}{\left[1 + b_{CO} P_{CO} + \sqrt{b_{H_2} P_{H_2}}(1 + K_3 b_{CO} P_{CO})\right]^2}, \quad (5)$$

where k_4 is the rate constant for the rate-limiting stage 4, K_3 the equilibrium constant for stage 3, and $b_i P_i$ are the products of the adsorption coefficients and the partial pressures of the reactants. Eqn. (5) describes quantitatively the experimental relations for all the catalysts which we have investigated and agrees with the kinetic results obtained in other studies.[86,87,93] The heats of adsorption q_{CO} of CO on metals, agreeing with the values of q_{CO} found by other procedures,[23] were calculated from the temperature variation of b_{CO}.[90,91]

The following expression for the process selectivity with respect to methane S_{CH_4} can be written on the basis of Scheme 8:[89,91,92]

$$S_{CH_4} = r_5/(r_5 + r_6) = [1 + (k_6 b_{CO} P_{CO}/k_5 \sqrt{b_{H_2} P_{H_2}})]^{-1}, \quad (6)$$

where r_i and k_i are the rates of stages 5 and 6 and the corresponding rate constants.

The selectivity with respect to higher hydrocarbons S_{C_n} is $1-S_{CH_4}$. Consequently

$$S_{C_n} = \frac{k_6 b_{CO} P_{CO}/k_5 \sqrt{b_{H_2} P_{H_2}}}{1 + (k_6 b_{CO} P_{CO}/k_5 \sqrt{b_{H_2} P_{H_2}})}. \quad (7)$$

Eqns. (6) and (7) lead to kinetic equations describing the processes involving the hydrogenation of CO to methane and higher hydrocarbons (the Fischer-Tropsch synthesis):

$$r_{CH_4} = rS_{CH_4}, \quad r_{C_n} = rS_{C_n}. \quad (8)$$

These expressions describe the experimental data satisfactorily.[89,91]

The rate of formation of individual hydrocarbons can be calculated from Eqn. (8) and the Schultz–Flory equation:[84]

$$c_n = n(1-\alpha)^2\alpha^{n-1}, \quad (9)$$

where c_n is the concentration of the hydrocarbon in which the number of carbon atoms is n. The coefficient α, which is usually found empirically from the proportions of the products,[84] is the probability of the formation of the higher hydrocarbon, i.e. the ratio of the rate of chain propagation (r_p) to the sum of the rates of chain propagation and termination (r_t):

$$\alpha = r_p/(r_p + r_t) = r_6/(r_6 + r_5). \quad (10)$$

The physical significance of the coefficient α follows from Eqn. (10). It consists in the fact that $\alpha = S_{C_n}$ in Eqn. (9):

$$\alpha = [1 + \beta(\sqrt{P_{H_2}}/P_{CO})]^{-1}, \quad (11)$$

where

$$\beta = k_5 \sqrt{b_{H_2}}/k_6 b_{CO}.$$

Thus the mechanism proposed for the hydrogenation of CO (Scheme 8) and the corresponding kinetic equation (5) make it possible to elucidate the significance of the coefficient α in terms of the rate (equilibrium) constants for the elementary stages.

V. The rules for the selection of ketone hydrogenation catalysts

1. Catalytic activity

The available data on the empirical selection of catalysts for the hydrogenation of carbonyl compounds are presented in a model review.[1] The mechanisms which we have established for the acetone hydrogenation reactions permit an approach to a rational selection and improvement of catalysts for the selective hydrogenation of carbonyl compounds.

It can be seen from the data in Table 3 that the specific catalytic activity r [the rate of reaction (I)] decreases in the sequence

$$\begin{aligned} &Pt/Al_2O_3 > Cu/Cr_2O_3 > Ni\ black > Ni/Cr_2O_3 > \\ &> Ir/Al_2O_3 > Rh/Al_2O_3 > Ni/Al_2O_3 > Ru/Al_2O_3 > \\ &> Cu/Al_2O_3 > Co/Al_2O_3 > Co\ black \gg Fe/Al_2O_3, Pd/Al_2O_3, Cu\ black. \end{aligned} \quad (XII)$$

The last three members of this series did not exhibit an activity in reaction (I); the causes of this have already been examined.[13,14]

The series (XII) agrees qualitatively with the activity series of metallic films found by Stoddart and Kemball:[44]

$$Pt > Ni > Fe,\ W > Pd > Au. \quad (XIII)$$

However, it is essential to note that the following problem arises when the metal activity series in low-temperature hydrogenation (and similar processes) are compared and interpreted. During these processes, there is no appreciable influence of the reaction medium on the catalyst, levelling out the differences between specimens of the same chemical composition but with different degrees of dispersion, as happens, for example, in many oxidation reactions[67] occurring at higher temperatures. The smaller the crystal size, the higher the coordinative unsaturation of the surface M centres and the greater their affinity for the reactants. This is indicated, in particular, by the increase in the heat of adsorption of acetone q_A with decrease in the average metal particle size $\bar{d}$ (Fig. 3). The latter agrees with the results of numerous quantum-chemical calculations,[94] showing that, on passing from small clusters to large crystals, the metal–metal cohesion bond is strengthened and the metal–adsorbate adhesion bond is weakened, saturation being attained in the region of approximately 10–20 nm. Relations of this kind are apparently characteristic of low-temperature "structure-sensitive" (in Boudart's terminology[95]) hydrogenation processes and other reactions.

With increase in the heat of adsorption of acetone, q_A, the adsorption entropy falls—the thermodynamic compensation effect occurs:[15,62] the higher the heat of adsorption, the more negative the entropy (ΔS^0_H) (the smaller the mobility of the adsorbed species). However, even in the presence of such an effect, the influence of the degree of dispersion of the metal on the acetone adsorption coefficient b_A is considerable (it vanishes only on passing to large crystals). The position of the metal in the activity series therefore depends both on its chemical nature and on the degree of its dispersion.

For "structure-sensitive" reactions such as the hydrogenation of the carbonyl group of ketones, the role of the degree of the dispersion of the metal may not be manifested solely in its influence on the energy of the bonds between the reactants and the surface. The probability of the multipoint adsorption of complex molecules of the compound hydrogenated and of the activated complexes may depend on the dimensions of the microcrystal (Fig. 2). Furthermore, account must be taken of the influence of the chemical nature of the crarier on the activity both as a consequence of the interaction of the metal with the carrier and of the activation of the substrate on the sections of the carrier adjoining the metal. The ability of the hydrogen adsorbed on the metal to migrate to neighbouring sections of the oxide carrier is well known.[96] This can explain the finding that the Cu/Cr_2O_3 catalyst, which has approximately the same adsorption coefficients b_A and b_{H_2} as Cu/Al_2O_3, is characterised by a significantly greater (by a factor of 40–50) rate constant k_L for the rate-limiting stage (Table 3).

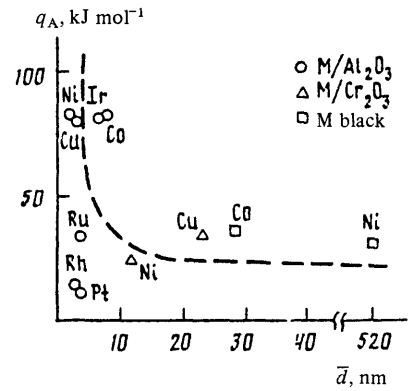


Figure 3. Dependence of the heat of adsorption of acetone on the degree of dispersion of the metal.

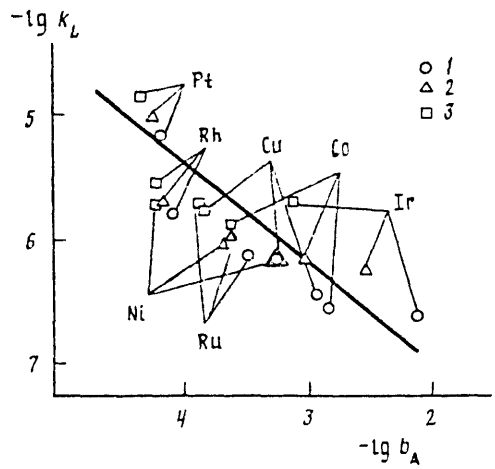


Figure 4. Dependence of the rate constant for the rate-limiting stage of the hydrogenation of acetone on the adsorption coefficient of acetone at different temperatures (K): *1*, 337; *2*, 348; *3*, 364.

In the case of metals deposited on the same carrier (γ-Al_2O_3) and having approximately the same degrees of dispersion ($\bar{d} \simeq 3$–7 nm), the specific catalytic activity r diminishes in the sequence

$$Pt > Ir > Rh > Ni > Ru > Cu > Co \gg Fe,\ Pd\ . \quad (XIV)$$

This series can be naturally interpreted on the basis of the mechanism proposed for the hydrogenation of acetone (Scheme 2). The bonds formed by the ketone and H_2 with the surface are ruptured in the rate-determining stage 3. One should therefore expect a decrease in the rate constant for the rate-limiting stage with increasing strength of the reactant–metal adsorption bond. Fig. 4 shows that k_L does indeed diminish with increase in b_A. b_A diminishes steadily, in its turn, with increase in the electronegativity of the metal χ_M (Fig. 5). This can be explained by the dominant role of the dative interaction in the formation of the adsorption π-complex (I): with increase in χ_M, the energy of this interaction falls, since the ability of the metal to give up electrons to the ketone molecule being adsorbed decreases.

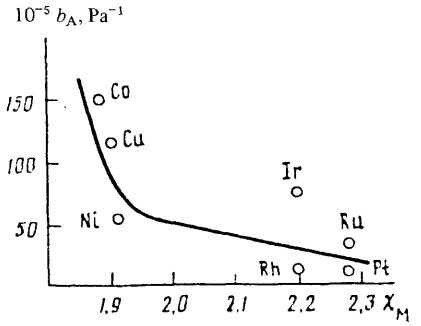


Figure 5. Relation between the adsorption coefficients of acetone (337 K) for metals deposited on Al_2O_3 and the Pauling electronegativities of the metals.

The fact that $\lg k_L$ is correlated satisfactorily solely with the strength of the acetone bond can be explained in the following manner. We formulate the Brønsted–Temkin equation for k_L:

$$k_L = gK_L^{\alpha}, \qquad (12)$$

where g and α are constants and k_L is the equilibrium constant for stage 3 (Scheme 2). In its turn, $K_L = b_{AH}K/b_A\sqrt{b}_{H_2}$ [b_{AH} is the adsorption coefficient of the semihydrogenated form $(CH_3)_2COH$ and K is the equilibrium constant, independent of the catalyst, of the gas-phase reaction $(CH_3)_2CO + 0.5H_2 = (CH_3)_2COH$]. Since the M–H bond is ruptured in stage 3 (Scheme 2) and the analogous M–C σ-bond is formed in the intermediate compound $(CH_3)_2C(M)–OH$, one can assume that the ratio $b_{AH}/\sqrt{b}_{H_2}$ changes little on passing from one metal to another. Therefore $K_L \simeq (\text{const.})b_A^{-1}$, so that

$$k_L = g\,(\text{const})\,b_A^{-\alpha} = (\text{const}')\,b_A^{-\alpha}. \qquad (13)$$

The transfer coefficient α can be found from the slope of the linear plot of $\lg k_L = f(\lg b_A)$ (Fig. 4). It proved to be 0.7, which is close to the typical value $\alpha = 0.5$.

In comparing the rates of the overall reaction (I) on different metals, one should use the kinetic equation (2), which can be put in the form $r = k\theta_A\theta_H$ (θ_A is the degree of surface coverage by acetone). Since saturation of the active centres Z_H by hydrogen ($\theta_H \simeq 1$) was attained in most cases for the conditions selected (Table 3), it follows that $r = k_L\theta_A$.

Consider the dependence of r on the heat of adsorption of acetone q_A. By differentiating $\ln r$ with respect to q_A and setting the derivative $d \ln r/dq_A$ equal to zero, we find [taking into account Eqn. (13)] the condition for the optimum $(\theta_A)_{opt} = 1 - \alpha$. This means that the highest rate of hydrogenation is attained for a degree of saturation at the centres Z_A by acetone equal to $1 - \alpha$. The optimum adsorption coefficient of acetone corresponds to this:

$$(b_A)_{opt} = [(\theta_A)_{opt}/(1 - (\theta_A)_{opt})]\,P_A^{-1} = [(1 - \alpha)/\alpha]\,P_A^{-1}.$$

The calculated quantity $(b_A)_{opt} = 4.3 \times 10^{-5}$ Pa^{-1} is close to the experimental value b_A for Pt (6×10^{-5} Pa^{-1} at 364 K), which explains why Pt occupies the first place in the series (XIV). For acetone–metal bond energies exceeding the optimum value, the activity should fall and, when $q_A < (q_A)_{opt}$ the activity should increase with increasing q_A, which is in fact observed in practice (Fig. 6).

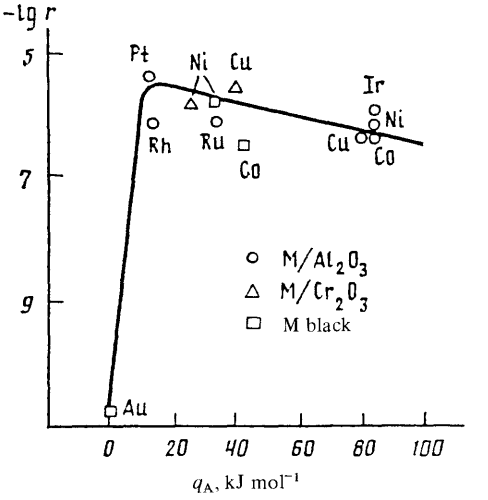


Figure 6. Dependence of the catalytic activities of metals in the hydrogenation of acetone at 364 K on the heat of adsorption of the ketone.

When cyclopentanone is hydrogenated on metallic films[97] the following metal activity series holds: Pt > Pd > Rh > W > Ni. It is in general similar to the sequences (XII) and (XIV) (with the exception of the position of Pd), which justifies the hypothesis that the rules established for the hydrogenation of acetone are fairly typical for the reactions of compounds of this class.

2. Selectivity

Together with hydrogenation reactions of type (I), the complete reduction of ketones with formation of the corresponding hydrocarbons [reaction (II)] can take place on metal catalysts. This process is analogous to the synthesis of methane from CO and H_2.

In the hydrogenation of acetone in the temperature range from 300 to 370 K on deposited metal, the formation of propane was observed[15] in the initial period of the reaction only on platinum (the selectivity with respect to C_3H_8 was 100%) and on iridium. In the latter case, propane and isopropyl alcohol were detected in the reaction products.

In catalysis on metallic films,[44] the activity of the metals in reaction (II) diminishes in the sequence

$$Pt > W > Ni > Fe \gg Pd, Au, \qquad (XV)$$

which resembles the activity series (XIV) in relation to the overall acetone hydrogenation process.

In order to interpret the selectivity with respect to C_3H_8, it is sufficient to supplement Scheme 3 by a complex stage involving further interaction of the adsorbed alcohol with the adsorbed H atoms:

$$6)\ Z_H(CH_3)_2CHOH + Z_HH \rightarrow (I) \xrightarrow[fast]{Z_HH} C_3H_8 + H_2O + 3Z_H,$$

where (I) is an intermediate compound.

Thus the selectivity with respect to the hydrocarbon is

$$S_{C_3H_8} = k_6\theta_H/(k_6\theta_H + k_5).$$

At fairly high pressures P_{H_2}, where $\theta_H \simeq 1$, we obtain

$$S_{C_3H_8} = [1 + (k_5/k_6)]^{-1}.$$

The constants k_5 and k_6 depend equally on the bond energy between the alcohol molecule and the surface, so that the ratio k_5/k_6 does not depend on this energy. At the same time, the constant k_5 is also independent of the M–H bond energy, whereas k_6 increases as this bond is weakened. Consequently the selectivity with respect to propane is given by

$$S_{C_3H_8} = [1 + \exp(\alpha q_{H_2}/2RT)\,(\text{const})]^{-1}. \qquad (20)$$

According to Eqn. (20), one should expect the formation of hydrocarbons in the hydrogenation of ketones on metals which bind hydrogen least strongly. Among the deposited catalysts tested in the acetone hydrogenation reaction, such metals are Pt, Ir, and Cu. The formation of propane on Pt and Ir only shows that an obligatory condition is also the involvement in stage 6 of atomic hydrogen (hydrogen is adsorbed on Cu in the form of molecules[43]).

The activity r of transition metals in relation to the overall acetone hydrogenation process diminishes with increase in the heat of adsorption of the ketone q_A (Fig. 6). Comparison of the values of q_A with known[23] values of q_{H_2} shows that q_A and q_{H_2} vary in general in parallel. The activity of the metal r therefore falls with increasing q_{H_2}. Since $S_{C_3H_8}$ also diminishes with increasing q_{H_2} according to Eqn. (20), one should expect a similarity between the overall metal activity series and the activity series in relation to reaction (II), which is in fact observed [cf the series (XIV) and (XV)].

The extensive hydrogenation of ketones is promoted by the presence of atomic hydrogen weakly bound to the metal surface. On passing from a deposited metal to a metal film, the strength of the M–H bond should diminish as a consequence of the increase in the size of the metal crystals. This can also be used to account for the finding that, in the case of metallic films, the formation of propane could be detected on a greater number of metals than on deposited catalysts having a high degree of dispersion.

It follows from Eqn. (20) that, with increase in temperature, the selectivity with respect to the hydrocarbon should increase, which is also in agreement with experimental data.[44]

VI. The rules for the selection of carbon monoxide hydrogenation catalysts

1. Catalytic activity

Data for the specific catalytic activities of a large number of transition metals in relation to the overall conversion of CO have been obtained in a number of studies.[86–88] The activities of metals deposited on Al_2O_3, measured at atmospheric pressure and 548 K,[86] decrease in the sequence

$$Ru > Fe > Ni > Co > Rh > Pd > Pt > Ir. \qquad (XVI)$$

The activity series for metals deposited on SiO_2 is somewhat different:[88]

$$Co > Fe > Ru > Ni > Rh > Ir,\ Pt > Pd > Cu. \qquad (XVII)$$

The data which we have obtained[98] for the specific catalytic activities of metal catalysts in relation to the hydrogenation of CO and also for their selectivities with respect to CH_4 are presented in Table 4. It is seen that at 548 K the activities of the metals deposited on γ-Al_2O_3 and having approximately the same degrees of dispersion (~2–7 nm) decrease in the sequence

$$Ru > Rh > Co > Ni > Pt > r > Pd \gg Fe, Cu. \qquad (XVIII)$$

In general the series (XVI)–(XVIII) are similar: among group VIII metals, the metals of the iron and ruthenium subgroups are the most active, while platinum, palladium, and iridium are least active. Activity series, analogous to the series (XVIII), established at atmospheric and elevated pressures have been described.[82,99]

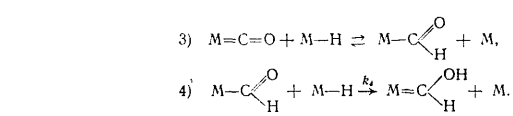
The catalytic activities of deposited cobalt catalysts in the Fischer–Tropsch synthesis at 540 K diminish in the following sequence of carriers:

$$SiO_2 > TiO_2 > ZrO_2 > BeO > Cr_2O_3 > Al_2O_3 > MgO \gg WO_3. \qquad (XIX)$$

At the same temperature, the activities of deposited nickel catalysts diminish in the sequence of carriers

$$ZrO_2 > TiO_2 > BeO > MgO > Al_2O_3 > SiO_2 > Cr_2O_3 \gg WO_3. \qquad (XX)$$

The variation of the activities of the metals in the sequence (XVIII) can be explained on the basis of the CO hydrogenation mechanism (Scheme 8). For this purpose, we specify in a more concrete form the chemistry of stages 3 and 4. If one begins with the assumption that the key intermediate compound ZX_O represents the adsorbed "enolic" form of formaldehyde,[82] the stages indicated can be formulated as follows:



At low temperatures, at which the activity series (XVIII) has been attained, the degree of surface coverage by CO molecules (θ_{CO}) is close to unity. Eqn. (5) then assumes the form

$$r = k_4 K_3 b_{H_2} P_{H_2} (b_{CO} P_{CO})^{-1}. \quad (14)$$

We shall consider the dependence of the constant of this equation on the heats of the stages, assuming that the entropy terms are approximately constant in a series of isotypical catalysts. It is also evident that

$$b_{CO}^{-1} \propto \exp(-q_{CO}/RT), \quad (15)$$

$$b_{H_2} \propto \exp(q_{H_2}/RT). \quad (16)$$

Since the M–H bond is ruptured and the M=C bond is partly ruptured, in stage 3, it follows that

$$K_3 \propto \exp(-q_{CO}/2RT - q_{H_2}/2RT). \quad (17)$$

We have the following expression for the equilibrium constant for stage 4:

$$K_4 \propto \exp(q_{CO}/2RT - q_{H_2}/2RT),$$

On the basis of the Brønsted–Temkin relation, we formulate the following expression for the rate constant for this stage:

$$k_4 \propto \exp(\alpha q_{CO}/2RT - \alpha q_{H_2}/2RT) \quad (18)$$

where α is the transfer coefficient, usually equal to 0.5.

On substituting Eqns. (15)–(18) in Eqn. (14) and taking into account the fact that the comparison is carried out at a constant P_i, we obtain (for $\alpha = 0.5$)

$$\ln r \propto -1.25(q_{CO}/RT) + 0.25(q_{H_2}/RT).$$

Since the absolute value of the numerical coefficient of q_{CO} is much greater than that of q_{H_2} and in addition $q_{CO} > q_{H_2}$,[23,42] one can write

$$\ln r \cong -1.25(q_{CO}/RT) + \text{const}, \quad (19)$$

i.e. the catalytic activity should decrease with increase in the heat of adsorption CO, which is confirmed qualitatively by the data in Fig. 7.

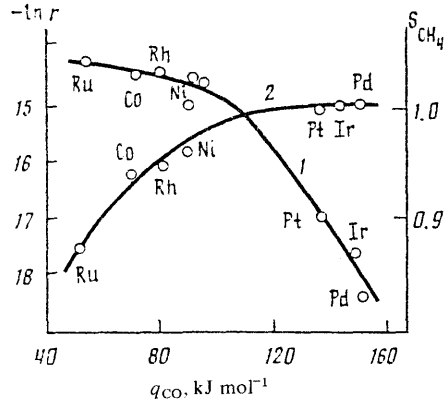


Figure 7. Dependence of the catalytic activities of metals (curve *1*) in the hydrogenation of CO and of their selectivities with respect to methane (curve *2*) on the heat of adsorption of CO.

In its turn, q_{CO} depends on the average metal particle size d: the smaller d, the greater q_{CO}. Evidently the influence of carriers [see the series (XIX) and (XX)] on the activity of a given metal is manifested primarily by a change in the degree of dispersion of the deposited metal M, on which depends the heat of adsorption of CO. With increase in $\bar{d}$, r initially rises, since this entails a decrease in q_{CO}, reaching a maximum in the presence of Co/SiO_2 ($\bar{d}$ = 38 nm) and Ni/ZrO_2 ($\bar{d}$ = 97 nm) (Table 5), but on further increase in $\bar{d}$, the M–CO bond is apparently weakened so much that r decreases in the presence of Co/TiO_2 ($\bar{d}$ = 46 nm) and Co/WO_3 ($\bar{d}$ = 60 nm). The same also applies to nickel catalysts: on Ni/TiO_2 ($\bar{d}$ = 103 nm) and Ni/WO_3 ($\bar{d}$ = 181 nm), r decreases. A similar dependence of the activity of the metal on the degree of dispersion was observed by Boudart and McDonald[68] and Kuznetsov et al.[100] Furthermore, the yield of oxygen-containing compounds (mainly ethanol) increased with increase in the degree of dispersion of cobalt deposited on the same carrier.[100]

The coefficient α in the Schultz–Flory equation also diminishes with increasing degree of dispersion of the metal. If account is taken of Eqn. (7) and the fact that q_{CO} increases as $\bar{d}$ diminishes, the dependences of r and α on $\bar{d}$ described above become analogous to the dependences of r and S_{C_n} on q_{CO} obtained whilst varying the chemical nature of the metal (Fig. 7).

2. Selectivity

It is seen from the data in Table 4 that the selectivity in the hydrogenation of CO to methane diminishes (and that with respect to higher hydrocarbons increases) in the following sequence of metal catalysts:

$$\text{Pd, Ir} > \text{Pt} > \text{Ni} > \text{Rh} > \text{Co} > \text{Ru}. \quad \text{(XXI)}$$

The selectivity with respect to higher hydrocarbons S_{C_n} of the CO catalyst diminishes in the sequence of carriers

$$ZrO_2 > MgO > BeO > Al_2O_3,\ Cr_2O_3 > SiO_2 > TiO_2 > WO_3 \quad \text{(XXII)}$$

and that of the nickel catalyst diminishes in the sequence

$$ZrO_2 > Al_2O_3 > Cr_2O_3 > MgO > BeO,\ SiO_2 > TiO_2 > WO_3. \quad \text{(XXIII)}$$

Comparison of the series (XVIII) with (XXI) shows that there is an antiparallel relation between the activity and the selectivity with respect to methane S_{CH_4}: the higher r, the smaller S_{CH_4} (Fig. 8). It has been shown in a study[92] where this empirical relation was noted for the selectivity with respect to CH_4 can be put in the form $S_{CH_4} = (1 + \eta)^{-1}$, where $\eta = r_6/r_5$ is the ratio of the rates of stages 6 and 5 in the CO hydrogenation mechanism (Scheme 8). Bearing in mind that, on passing from one metal to another, the changes in η are associated mainly with the changes in the rate constants (k_6 and k_5) for the stages indicated and the formation of ZX_0' and ZX_1 does not involve the appearance of new bonds with the catalyst (H which adds to the adsorbed species of CO is inserted in the M–C bond), we obtain[92,98]

$$S_{CH_4} = [1 + \text{const}' \cdot \exp(-\alpha q_{CO}/RT)]^{-1} \quad (21)$$

(it is assumed that the changes in q_{CO} predominate over the changes in q_{H_2}). It follows from Eqn. (21) that the selectivity with respect to CH_4 should increase (whilst that with respect to higher hydrocarbons should diminish) with increase in q_{CO}, which is in fact

actually observed (Fig. 7). Simultaneous solution of Eqns. (19) and (21) leads (after the elimination of q_{CO} from them) to the expression[92,98]

$$S_{CH_4} = (1 + Br^c)^{-1} \quad (22)$$

(B and c are constants). Eqn. (22) explains the observed antiparallel variation of the activity S_{CH_4} (Fig. 8). Furthermore, it follows from Eqn. (22) (in conformity with experimental data) that $S_{CH_4} \to 1$ when $r \to 0$ and $S_{CH_4} \to 0$ when $r \to \infty$.

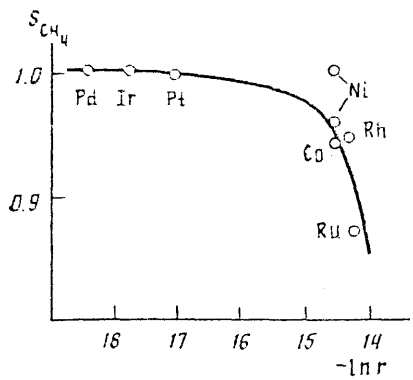


Figure 8. Relation between the activities and selectivities of metals in the CO hydrogenation reaction.

The relations examined refer to the case where the normal Schultz–Flory distribution holds and when the carrier of the metal can be regarded as inert.

For the same metal deposited on different carriers [see the series (XXII) and (XXIII)], the changes in q_{CO} are due to different degrees of dispersion of the metal, so that according to Eqn. (21) a dependence of S_{C_n} on $\bar{d}$ is also to be expected, which has in fact been observed for both cobalt and nickel catalysts (Table 5). However, the changes in S_{C_n} are not induced solely by changes in the degree of dispersion of the metal and hence by the different values of q_{CO}. In each group of catalysts, deposited on different carriers (Table 5), it is possible to differentiate M/L specimens (L is the carrier) having virtually the same degrees of dispersion and hence the same heats of adsorption q_{CO}. At the same time, the selectivities S_{C_n} of such catalysts differ by 24–34%, which means that the subsequent reactions of the intermediate ZX_0 take place with a direct involvement of the carrier particles (apparently at the metal–carrier interface[101]).

In conformity with the mechanism of the hydrogenation of CO (Scheme 8) it has been suggested that the hydrocarbon chain grows via the interaction of the adsorption complex of ZCHOH (ZX_0) with ZCO. Under these conditions, the complex ZCHOH can be partly bound to the carrier (Lewis acid) as a result of the interaction of the unshared electron pair of the oxygen atom with the carrier cation (M_1^{n+}):

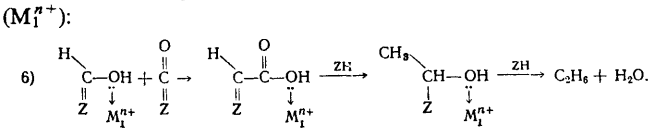


Table 5. Specific catalytic activities and selectivities of deposited metal catalysts in the hydrogenation of CO.

Carrier	$\bar{d}$ for metal, nm	$10^7 r^*$, mol m^{-2} s^{-1}	Selectivity w.r.t. higher hydrocarbon S_{C_n}, %
CO catalyst			
SiO_2	38	52	26
TiO_2	46	9.0	17
ZrO_2	33	8.4	50
BeO	18	5.5	38
Cr_2O_3	15	5.3	30
Al_2O_3	6	4.3	30
MgO	3	1.0	46
WO_3	60	<1	0
Ni catalyst			
ZrO_2	97	262	66
TiO_2	103	54	32
BeO	21	27	36
MgO	1	23	43
Al_2O_3	2	11.4	54
SiO_2	6	3.2	36
Cr_2O_3	12	1.9	44
WO_3	181	<1	0

Note. Mixture composition: P_{CO} = 20 kPa, P_{H_2} = 50 kPa.

* Obtained at 540 K.

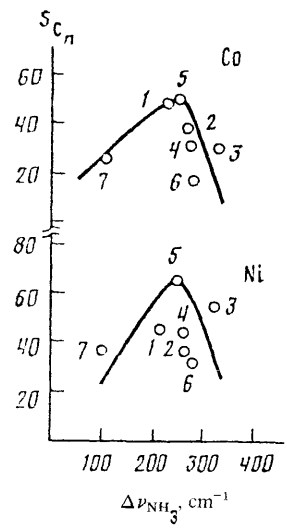


Figure 9. Dependence of the selectivities of deposited Ni and Co catalysts on the acidity of the carriers; carrier: *1*, MgO; *2*, BeO; *3*, Al_2O_3; *4*, Cr_2O_3; *5*, ZrO_2; *6*, TiO_2; *7*, SiO_2.

Then the rate of stage 6 and hence S_{C_n} should depend on the acidity of the carrier. Experimental data have shown that such a relation does indeed exist (Fig. 9): with increase in acidity [with increase in the vibration frequency of the ammonia adsorbed on $(M_1^{n+})_x O_y$ 102], the selectivity with respect to higher hydrocarbons also increases, reaching a maximum for M/ZrO_2. Further increase in the acidity of the carrier diminishes S_{C_n}, the catalyst deposited on carriers with the maximum acidity (M/WO_3) exhibiting 100% selectivity with respect to CH_4. The existence of the optimum acidity can be explained by the fact that, when the bond between the

complex ZCHOH and M_l^{n+} is both too strong and too weak, the probability of the hydrocondensation process is reduced.

In this case the following relation can be written for the selectivity of the Fischer–Tropsch synthesis:

$$S_{C_n} = S_{C_n}(q_{CO}) + S_{C_n}(q_L),$$

where $S_{C_n}(q_{CO})$ is the contribution to the selectivity determined solely by the heat of adsorption of CO and $S_{C_n}(q_L)$ is the contribution to selectivity which depends on the energy of the acid–base interaction.

VII. Hydrogenation of aldehydes

The hydrogenation of saturated aldehydes is of practical importance for the preparation of primary alcohols, mainly 1-propanol, 1-butanol, isobutyl alcohol, and certain higher alcohols:

$$R{-}CHO + H_2 = R{-}CH_2OH. \qquad \text{(XXIV)}$$

Reaction (XXIV) is the concluding stage of the preparation of alcohols by oxo synthesis from alkenes, CO, and H_2. The hydrogenation reaction is carried out as a rule on the catalyst (CO/kieselguhr) used for oxo synthesis. In addition, the Ni–Cu–Cr[103] and Cu–Zn–Al catalysts (synthesis of methanol from CO and H_2),[104] the Ni–Cr and Cu–Cr catalysts,[105] as well as mixed catalysts based on platinum metals[106] are used for the hydrogenation of aldehydes. The detailed mechanism of reaction (XXIV) has not been investigated.

VIII. Conclusion

Certain generalisations, necessary for the rational selection of catalysts and the prediction of the catalytic activity of substances in the hydrogenation of different carbonyl compounds and CO may be based on the data described in this review for the mechanisms and kinetics of such reactions. The activity and selectivity of metal catalysts depend significantly on the energy of the bond (q_R) between the molecule hydrogenated, R, and the catalyst. While the general character of the variation of the catalytic activity with the metal–R bond strength is similar, the optimum values of q_R depend significantly on the nature of the molecule hydrogenated: $(q_{CO})_{opt} \gg (q_{ketone})_{opt}$. As a result of this, an antiparallel variation of the activities of transition metals as a function of their positions in the Periodic Table is observed for the ketone and CO hydrogenation reactions.[107]

The quantity q_R may be varied by altering either the chemical nature of the metal or the degree of its dispersion. The size of the crystals can be regulated in its turn by introducing various additives[107] or by varying the conditions in the reduction of metal oxides.[61]

Consequently, for "structure-sensitive" hydrogenation reactions of carbonyl compounds and CO, where the differences between the adsorption and catalytic activities are not abolished under the influence of the reaction medium, the unequal degrees of dispersion of the metal have just as strong an influence on the catalytic properties as the chemical nature of the metal. Another factor determining the activity and selectivity of the deposited metals may be the variation of q_{CO} under the influence of the "strong metal–carrier interaction" (SMCI).[108,109] The SMCI effect is manifested as a rule for small values of $\bar{d}$ (< 2 nm[109]) and when the carrier cations M_l^{n+} are able to undergo a change in the oxidation state.

The selectivity of the hydrogenation of carbonyl compounds depends to a large extent on the form of the adsorption of the molecule hydrogenated, which is in its turn determined by the chemical composition of the catalyst. Thus, when the "planar" π-complex (I) is formed, acetone is hydrogenated only as far as isopropyl alcohol, while the transition to the "perpendicular" alkoxy-structure (II) promotes the complete reduction of ketones to hydrocarbons.[69]

The CO molecule is also adsorbed in different forms depending on the nature of the catalyst. On transition metals, where carbon monoxide can form bridged and linear structures [see reaction (X)], the carbon–oxygen bond is weakened as a consequence of the predominance of the dative bond.[110] The main CO hydrogenation products on transition metals are therefore hydrocarbons. Among transition metal (Ni, Cu, Zn, Cr) oxides, the preferential formation of oxygen-containing compounds is observed. This reaction pathway is determined by the formation of the CO–M_xO_y donor–acceptor bond. In this case, the C–O bond is seen to be strengthened and the M–C bond is weakened.[110]

The general features of the selective heterogeneous-catalytic hydrogenation reactions of carbonyl compounds and CO listed above will help in the future to achieve a general treatment of new experimental results concerning particular reactions and alternative bases for the specific rational choice of selective catalysts for these processes.

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